Green Energy and Technology

Malti Goel
M. Sudhakar *Editors*

Carbon Utilization

Applications for the Energy Industry

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This book is dedicated to Dr. Vasant R. Gowariker Eminent Space Scientist and Great Mentor

Foreword

The Inter-governmental Panel on Climate Change (IPCC) assessment of 2014 (AR5) suggests that the carbon dioxide concentrations in the atmosphere are approaching 400 ppm, against the pre-industrial value of 280 ppm. A safe limit of 450 ppm has been set for the year 2050 to protect the planet Earth from any climatic disasters. With the growing threat of climate change resulting from increasing accumulation of CO_2-eq gases, CO_2-sequestration technology is seen as an assurance for continuation of fossil fuels use, especially coal in the energy sector.

To do this we must have adequate research and policy infrastructure that can help in testing CO_2 sequestration and utilization options. When Dr. (Mrs) Malti Goel, who was Adviser in the Department of Science & Technology, Government of India approached me to inaugurate the five-day training workshop on carbon capture, storage and utilization, organized by Climate Change Research Institute, I readily agreed. She is the founder of the institute. I have strongly felt that we need to establish a pilot-scale facility on CO_2 capture to test all the research results from chemical and physical processes at one place in the country. Our laboratory at CSIR-Indian Institute of Petroleum, Dehradun, as well as other institutions in India has reported exciting results from the research carried out and such a facility will help in upgrading our research output.

I am happy that the book Carbon Utilization: Applications for the Energy Industry edited by Malti Goel and M. Sudhaker has come out as an enthusiastic directive for research in terrestrial and bio-sequestration options and CO_2 utilization as a low carbon growth strategy for the industry. There is a wide coverage of topics in the 19 chapters of the book. New applications for the aluminum, steel, cement and fertilizers industries are incorporated. Although these topics may represent only a small segment of many possibilities that exist, they amply illustrate the importance of CO_2 utilization research and the way this field is advancing globally. I am sure that the readers will get an insight into perspectives of this emerging research area of energy technology.

Indeed bridging the gap between research and industry in CO_2 utilization is a fundamental challenge, which the scientific community must face. In this context the book should serve as a valuable knowledge bank to help policy makers, scientists, researchers and professors. I would be a medium for sharing novel ideas with industry as well as for induction of new coordinated research. I am glad that Springer is bringing out this under their Green Energy and Technology series.

Dr. Madhukar O. Garg, Ph.D., FNAE
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Preface

> *For a successful technology, reality must take precedence over public relation, for nature cannot be fooled.*
>
> —Richard Feynman, 1986

It is well known that the atmospheric carbon dioxide cycle (*carbon cycle* in short) has a vital role in maintaining the earth's dynamic system, components of that act on different time scales varying from less than a second to hundreds of years. Increasingly CO_2 is being added in the atmosphere from growing use of energy and its generation from fossil fuel combustion. This is affecting the natural carbon cycle, resulting in the global warming threat and climate change. Thus, the motivation for capturing carbon dioxide and storage comes from developing ways to remove excess carbon dioxide in the atmosphere for climate control.

The geo-engineering approach to climate change mitigation comprises 'removal of carbon dioxide' from the atmosphere as well as 'management of solar radiation' for controlling the global warming. The mechanics of reflecting part of the radiation back to space thereby preventing it to enter the earth's atmosphere is being worked out for the management of solar radiation. In this book we are focusing on carbon dioxide removal (CDR) processes. Sequestration of carbon dioxide by capture and storage or utilization into value-added products and energy fuels remains one of the most researched options for removal of excess carbon dioxide getting accumulated in the atmosphere.

The book 'Carbon Utilization—Applications for the Energy Industry' is the outcome of a capacity-building event held in India. It has appealing coverage of environment and engineering disciplines, viz. CO_2 abatement and utilization, CO_2 management in the industry towards a low carbon growth, CO_2 terrestrial sequestration and biotic options among others, for reducing carbon footprints in the atmosphere.

Scope

The book on carbon utilization incorporated invited lectures delivered at the workshop on awareness and capacity building, *Carbon Capture, Storage and Utilization: Towards low carbon growth Strategy*, held in New Delhi from July 27–31, 2015. Topics that could not be presented in the workshop, but proposed, are also included. The workshop was held by Climate Change Research Institute to highlight Indian contribution and has provided multidisciplinary perspectives for academic exchange of current research in the field of anthropogenic CO_2 sequestration and utilization as well as its application.

Although in a major policy shift, India has set a national target of achieving 175 GW installed electricity capacity from renewable energy sources by 2022 with solar energy having a major share of 100 GW, coal has been the backbone of India's electricity. India is the third largest producer and consumer of coal in the world and it is anticipated that coal continues to be dominant fuel in the coming decades for achieving the energy security. Yet we do not know how the coal use will take shape. Adoption of clean coal technologies and carbon sequestration as end-of-pipe solution provide low carbon pathways. Environment *cess* of INR 400 per tonne of coal use has been implemented as a policy imperative. A few questions therefore arise: whether to target use of renewable energy as the source of entire electricity (which would require huge investment), or to continue using fossil fuels and convert captured CO_2 to chemicals/fuels/plastics as it would make use of existing infrastructure to great extent? At the same time, what new conversion processes become possible in future with minimum energy consumption? Can we think of conversion of captured CO_2 directly into electricity in an electrochemical cell or its conversion to *graphene* which could eventually replace silicon chip? The solution of these would emerge with the application of science and technology to carbon capture and utilization. The possibilities are immense, a collection of state-of-the-art scientific reviews and research perspectives on carbon management strategies of relevance to the energy industry are presented in the book.

Already CO_2 sequestration and utilization are on the research agenda globally. National governments are investing heavily in carbon capture and utilization (CCU) research and there are significant ongoing research programmes worldwide. Innovations are taking place and reuse of waste CO_2 into valuable products is seen as not only environment savior, but also a step towards *circular economy*. Economics of CO_2 utilization would succeed in foreseeable future depending upon the purity and process used.

In the post-Kyoto phase, international protocols such as Paris Agreement on Climate Change have been signed by 175 countries (including European Union as one) in the 21st Conference of Parties meeting of the United Nations Framework Convention on Climate Change (UNFCCC) during December 2015. This protocol along with UN Sustainable Development Goals (SDGs) adopted in September 2015 give ample evidence of CO_2 sequestration linkages as a low carbon growth business strategy.

Structure of the Book

CO_2 sequestration and environment protection demand green energy and green technology. The book on Carbon Utilization has 19 chapters grouped into four sections namely:

I. CO_2 Emission, Sequestration and Utilization
II. Terrestrial Sequestration Options
III. Low Carbon Growth Strategy from CO_2 Utilization
IV. Current Research and Green Technology Perspectives for Industry

Part I covers a policy issues for energy and environment security in India. There is a need for all energy sources with the advancement in technology for fulfilling basic needs of people. Chapter 1 provides an overview of trends in carbon emissions, geo-engineering solutions and carbon dioxide capture and removal processes as well as the need for capacity development in this emerging technology. Experience from Indian Power industry for reducing carbon footprints is shared in Chap. 2. Chapter 3 proposes a Green Power Mission by way of clean energy technology development from renewable sources as well as coal based generation with CCS, for achieving a low carbon growth.

Part II covers research on terrestrial sequestration options in Chaps. 4–8. Chapter 4 is about the need for information on the spatial distribution of soil type for advancement of appropriate management techniques for carbon sequestration at the national level. In Chap. 5 authors further examine the soil carbon stock and soil CO_2 flux in the different terrestrial ecosystems, i.e. forest, bamboo and grasslands and relates it to land use patterns in north-east region of India. Chapters 6 and 7 provide assessment of the biomass potential plant species at different altitudes and in the coastal zone for regulating the carbon pool in these regions, respectively. A detail review of enzymatic CO_2 capture potential and current research in advancements made in the production of recombinant carbonic anhydrase is provided in Chap. 8.

In Part III Chaps. 9–14 describe CO_2 utilization as a low carbon growth strategy for India. The CO_2 chemical and biological conversion routes, innovative chlathrate hydrates to cage CO_2 and CO_2 injection in earth reservoirs for enhanced recovery of fuels are the research topics explained by the leading scientists and technocrates from an Indian perspective. Challenges of enhanced oil recovery in oil fields in India, strides made in enhanced coal belt methane recovery, recent success of CarbFix demonstration project in Iceland in June 2016 for utilization of CO_2 through accelerated mineralization in basaltic rocks and need for introduction of oxy fuel combustion of coal as a low carbon strategy for India are some of the important highlights.

Part IV of the book is on current research and green technology perspectives in energy industry covered in five chapters. Chapters 15–19 present technology advancement taking place in aluminum, steel and cement industry for mitigation of greenhouse gases. Exciting results from national companies in India are presented and the experiences are shared. Carbon footprint of Aluminum industry and perspectives for carbon neutrality through R&D measures is the theme of Chap. 15. Chapter 16 explains result of a pilot plant at a National Aluminum industry in India for micro-algae based CO_2 capture to create accelerated carbon sink. Critical scientific inputs and strategies are required for achieving CO_2 reduction in iron and steel industry by technology management. In Chap. 17 emerging technology solutions for carbon reduction in steel production are dealt. Chapter 18 covers approach to mitigation of carbon emissions in cement production through application of new technology. More efficient CO_2 capture using ammonia process in the Indian context is explained in Chap. 19.

The views expressed are those of authors. It is hoped that whether you are a student of science, researcher, postdoctoral fellow, professor, or policy planner or in industry you would surely find the book Carbon Utilization as an Indian contribution inspiring, educating and motivating.

Acknowledgements

We would like to convey our profound gratitude and appreciation to all renowned authors and contributors for their strong engagement and commitment. We also take this opportunity to thank members of review team especially Prof. Satyanarayana, Delhi University and Dr. V.A. Mendhe, CIMFR for their time and valuable help.

The book on carbon utilization could not have happened without the workshop on awareness and capacity building. We thankfully acknowledge and express our sincere thanks to Ministry of Earth Science, Government of India and ONGC Energy Centre for providing financial support for the workshop organized by Climate Change Research Institute (CCRI). We also convey our thanks to Dr. J. S. Sharma, Head of Environment Division, ONGC, Dr. Anupam Agnihotri, Jawaharlal Nehru Aluminium Research Development and Design Centre, Nagpur, Dr. V.A. Mendhe, CSIR-Central Mining and Fuel Research Institute, Dhanbad and Prof. Tapas Bhattacharyya, International Crops Research Institute for the Semi-arid Tropics, ICRISAT Development Centre, Patancheru for extending support.

We are indebted to Dr. M.O. Garg, Director General, CSIR who graced the workshop and delivered the inaugural address; Shri. M.P. Narayanan, former CMD Coal India and Dr. Jyoti Parikh, ED, IRADE who delivered special addresses. We express our gratitude to Dr. Anupam Agnihotri, Director, Jawaharlal Nehru Research, Design and Development Centre, Nagpur for the Keynote address on *CO_2Management—Indian Aluminium Industry Perspective* and Dr. B. Bhargava, Director General, ONGC Research Centre who also spoke in the inaugural session. Our thanks are to Shri R.K. Sachdev, Former Adviser, Ministry of Coal for steering the workshop concluding session.

We benefitted from the wisdom and insights of Prof. D.P. Agrawal, Chairman, Governing Council, Climate Change Research Institute, and its members especially Prof. V.S. Verma and Shri Gautam Sen for their heartening support. We extend our sincere thanks to Shri L.K. Bansal, Dr. Neha and Shri Anish Tripathi as well as

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Last but not least Swati Meherishi, Executive Editor, Applied Science & Engineering, Springer and her team deserves to be praised for their constant support.

New Delhi, India Malti Goel
Kochi, India M. Sudhakar
September 2016

Annexure

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- Central Power Research Institute, Bangalore
- Climate Change Research Institute, New Delhi
- CSIR-National Geophysical Research Institute, Hyderabad
- CSIR-Central Institute of Mining and Fuel Research, Dhanbad
- Dayal Singh College, Delhi
- Delhi University, South Campus, Delhi
- Department of Education, Delhi
- ICRISAT Development Centre, Telengana
- Jamia Hamdard, Delhi
- Jawahar Lal Nehru University
- Jawaharlal Nehru Aluminium Research Development and Design Centre, Nagpur
- Jupiter Oxygen Corporation, USA
- Manipur University, Imphal
- Maulana Azad National Institute of Technology, Bhopal
- National Fertilizers Limited, Vijaypur
- National Thermal Power Corporation, Noida
- Oil & Natural Gas Corporation (ONGC) Energy Centre, Delhi
- Oil & Natural Gas Corporation (ONGC), New Delhi
- Tamilnadu Agriculture University, Trichy
- Tata Steel, Jamshedpur
- The Energy and Resources Institute (TERI), New Delhi
- University of Calcutta, Kolkata

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Editors and Contributors

About the Editors

Dr. (Mrs.) Malti Goel is a physicist, former Adviser & Scientist 'G', Ministry of Science and Technology, Government of India and was affiliated with the Centre for Studies in Science Policy Studies, JNU and the Indian National Science Academy (INSA) as Emeritus Scientist. She obtained her Bachelor’s and Master’s degrees in Physics at the Birla Institute of Technology & Science (BITS), Pilani, and received D.I.I.T. Solid State Physics and Ph.D. in Physics from another premier institute, the Indian Institute of Technology (IIT), Delhi. She is a recipient of gold medal in M.Sc. Physics and a topper in D.I.I.T. As Research Associate at the Center for Materials Science, IIT Delhi her research on polymers and dielectrics has been published in international journals and was cited in patents. She has 26 years of experience in science administration in the Department of Science & Technology (DST) and has served on a number of programme advisory committees and other national committees for the promotion of thrust area programmes in the physical sciences and atmospheric sciences research in India, Dr. Malti Goel headed the Science & Technology Advisory Committee Division and represented on several Science & Technology Advisory Committees in the Socio-Economic Ministries and the Environment Ministry of Government of India. She was instrumental in catalyzing joint R&D projects with them at the national level. Her work has led to recognitions and many awards including Er. Abinash Chandra Chaturvedi Medal 2006 for Excellence in Environment Science & Technology, Bharat Jyoti Award in 2012 and the Build India Corporate Award in 2015. She represented India as Vice-Chair to the Technical Group of the International Carbon Sequestration Leadership Forum (CSLF) (2006–2008). She was invited to the official ceremony for the award Erice-Science for Peace 2006 held in the Vatican, Rome. She served as Science Diplomacy Ambassador for the Energy Workshop—2013 of The Third World Academy for Advancement of Science in developing countries, Trieste. She authored the first book ‘Energy Sources and Global Warming’ in 2005 and has since contributed several books and published 240 scientific papers in journals of international repute and conferences. She has also served on a number of high-level scientific committees and in the board of important professional bodies in India. Dr. Malti Goel received the Life Time Achievement Award 2016 in Climate Change Research bestowed by Pearl Foundation for Educational Excellence.

Dr. M. Sudhakar Scientist-G, Ministry of Earth Sciences, New Delhi, is currently the Director of the CMLRE. Dr. Sudhakar received his Ph.D. from the Indian School of Mines, Dhanbad and a Master’s degree in Law of the Sea and Marine Policy in 1990 from the London School of Economics & Political Science, UK as a British Council Fellow. Dr. Sudhakar served two of

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Part I

CO_2 Emission, Sequestration and Utilization: A Policy Dilemma for Energy Security

Chapter 1
CO_2 Capture and Utilization for the Energy Industry: Outlook for Capability Development to Address Climate Change in India

Malti Goel

Abstract Carbon dioxide and other greenhouse gas emissions are potential global warming threats and are accepted physical manifestations of increasing anthropogenic and development activities around the globe. Carbon dioxide (CO_2) having the highest contribution in it, understanding of its mitigation pathways is important for combating global warming and climate change. This paper on CO_2 sequestration and utilization for energy security in six sections is divided in two parts. We begin with natural carbon cycle, increasing carbon dioxide emissions from the energy sector, and the need for removal of excess carbon dioxide in the atmosphere. Among various geo-engineering approaches, carbon capture, storage and utilization comprises of carbon dioxide removal (CDR) - a land engineering technique for climate control and carbon dioxide utilization (CDU) through direct and indirect routes - a move for closing the carbon cycle toward a low carbon growth strategy. Several CO_2 reuse applications have come up for the energy industry. In part 2 of the paper, we present an overview of the existing initiatives by international and national agencies towards capability development. To address the challenges of capacity building in the emerging energy technology, a series of awareness workshops for researchers in academia and industry were organized in India. The contents of present book as an outcome of an awareness and capacity building workshop held in 2015 are covered. This chapter oversees latest developments, serves as Introduction to the book as well as presents the case for strengthening CO_2 utilization research in India and makes policy advocacy recommendations. The need for a CCU-Net India is highlighted.

Keywords Carbon dioxide removal · Carbon capture and utilization · India · Energy industry · Capacity building · Policy advocacy

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Abbreviations

CDR	Carbon dioxide removal
CDU	Carbon dioxide utilization
CCU	Carbon capture and utilization
IPCC	Intergovernmental Panel on Climate Change
CCS	Carbon capture and storage
CCSU	Carbon capture, storage & utilization
LCGS	Low carbon growth strategy
UNIDO	United Nations Industrial Development Organization
UNFCCC	United Nations Framework Convention on Climate Change
GHG	Green house gas
INDCs	Intended Nationally Determined Contributions
PSA	Pressure swing adsorption
GCCSI	Global Carbon Capture and Storage Institute
EOR	Enhanced oil recovery
ECBMR	Enhanced coal bed methane recovery
DME	Di-Methyl either
CDUUK	UK centre for carbon dioxide utilization
LCA	Life cycle analysis
GWP	Global warming potential
MEG	Monoethylene glycol
APEC	Asia Pacific Economic Corporation
CSLF	Carbon Sequestration Leadership Forum
CBTF	Capacity building for emerging economics task force
CDF	Capacity Development Fund
COPs	Conference of Parties
CDM	Clean Development Mechanism
SDGs	Sustainable Development Goals
DST	Department of Science & Technology
NTPC	National Thermal Power Corporation
ONGC	Oil and Natural Gas Corporation
TERI	The Energy Resource Institute
R & D	Research & Development
BHEL	Bharat Heavy Electrical Limited
NALCO	National Aluminum Co.
IFFCO	Indian Farmers Fertilizers Cooperative Limited
NFCL	Nagarjuna Fertilizers and Chemicals Limited
ACBCCS	Awareness and capicity buildings in carbon capture & storage
MNIT	Maulana Azad National Institute of Technology
DMC	Di-methyl carbonate
MEA	Mono ethanol amine
IEA	International Energy Agency
ICRISAT	International Crops Research Institute for the Semi-Arid Tropics
MHI	Mitsubishi Heavy Industries Ltd.

SBSTA	Subsidiary Body for Scientific and Technological Advice
NETL	National Energy Technology Laboratory
CSIR	Council of Scientific & Industrial Research

1 Introduction

Carbon dioxide and other greenhouse gas emissions are potential global warming threats and are accepted physical manifestations of increasing anthropogenic and development activities around the globe. Carbon dioxide (CO_2) having the highest contribution in it, understanding of its mitigation pathways is important for combating global warming. The atmospheric carbon dioxide cycle (carbon cycle in short) has a vital role in maintaining the balance in the earth dynamic system. Exchanges among the atmosphere, land, and oceans take place continuously (Fig. 1) and act on different time scales varying from less than a second to hundreds of years. Increasingly, CO_2 is being added in the atmosphere for meeting the growing energy demand and its generation from fossil fuels combustion. This is affecting the natural carbon cycle.

The global total and India's CO_2 emission profiles indicating trend from 1750 to 2010 are depicted in Fig. 2. Fossil fuels which were meeting 81% of world energy needs in 1990 are expected to provide 60% share in the primary energy by 2040 (IEA 2015). Globally coal continues to be the fuel of the future and is much needed for the energy industry. The CO_2 atmospheric concentrations have increased from 280 ppmv in

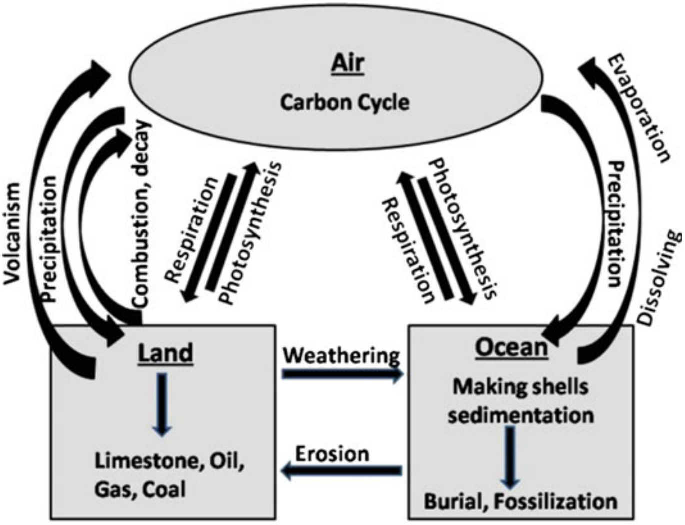


Fig. 1 The natural carbon cycle on Earth (*Source* adapted from http://www.astronomynotes.com/solarsys/s11.htm)

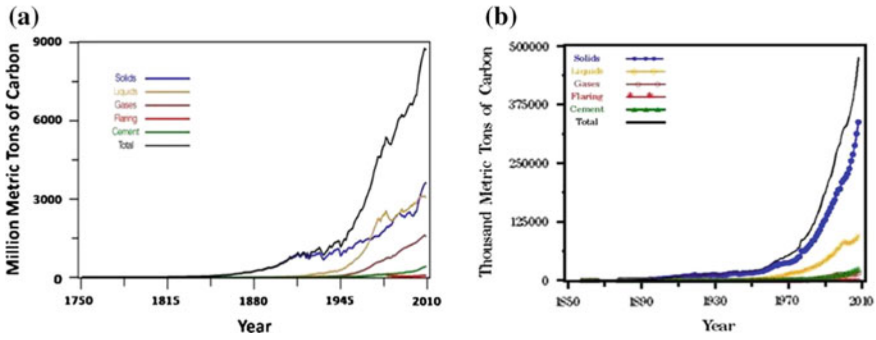


Fig. 2 **a** Global total CO_2 emissions and **b** analytical trends of CO_2 emissions from developmental activity in India (*Source* Marland et al. 2007)

preindustrial times to 374 ppmv in 2005 and to 396 ppmv in 2013 with a rise in average temperature by 0.84 °C. Evidence from Intergovernmental Panel on Climate Change (IPCC) has demonstrated that to limit global temperature rise to 2 °C above the average, the concentration of CO_2 equivalent greenhouse gases should not increase beyond 450 ppmv in the year 2050. Consequently the motivation for developing ways to remove excess carbon dioxide in the atmosphere by application of geo-engineering approaches comes from having a reasonable chance of achieving this target.

The IPCC fourth Assessment report—AR4—has defined geo-engineering solutions as ‘technological efforts to stabilize climate system by direct intervention in the energy balance of the earth for reducing global warming.’ Further to this The Royal Society stated it as a ‘deliberate large-scale manipulation of the planetary environment to counteract anthropogenic climate change.’ Geo-engineering solutions therefore comprise both the options of ‘removal of excess CO_2’ as well as ‘management of solar radiation’ (Crutzen 2006; Shephard 2009; Ming et al. 2014).

These would engross land, ocean as well as atmospheric engineering processes and techniques on the earth for balancing CO_2 concentrations in the atmosphere. Among these CO_2 sequestration—carbon capture, storage, and utilization (CCSU) is an emerging energy technology. The CCSU is understood as capturing CO_2 from its point sources and its storage into underground reservoirs and/or its utilization into value added chemicals and fuels. It is a potential low carbon growth strategy (LCGS) for the energy industry (UNIDO 2011) and may contribute up to 14% of the reduction in emissions by 2050 (IEA 2015). Science & technology has an important role in finding solution for climate change control. Soon after the 1992 Rio Earth Summit, there have been research programs undertaken in USA, Japan, and other countries to develop scientific methods of CO_2 sequestration (Herzog and Drake 1996; Chakma 1997).

We present this paper in two parts. We first discuss the geo-engineering approach to balance the carbon cycle. Next it describes status of carbon dioxide removal (CDR) and carbon dioxide utilization (CDU) processes. To avoid all underlying risks involved in CCS through CO_2 storage, the current shift to carbon capture and utilization (CCU) in the energy industry is expected to partially offset high cost of CO_2 capture. In view of rapid developments taking place we need inputs from diversified fields and basic understanding of these through capacity building. In the part 2 of the chapter we present an overview of capacity building initiatives by international and national agencies. This part also covers Contents of the book and the need for a CCU network in India. Finally, recommendations are made with conclusions. The improvement in energy efficiency of coal plants from use of advanced combustion cycles and replacement of fossil fuels by renewable sources are other options *not* covered here. These are dealt in Chaps. 2 and 3 of the book.

1.1 CO_2 Emissions from Developmental Activity—Global and India

International convention on climate change namely; United Nations Framework Convention on Climate Change (UNFCCC) was established in 1992. It came into force in 1994 and till date has been signed by 196 countries. Kyoto Protocol aimed to achieve 'stabilizations greenhouse gas concentration in the atmospheres at a level that could prevent dangerous anthropogenic interference with the climate system' was the first climate change global agreement proposed in 1997 and came into force only in 2005. Kyoto Protocol is binding for all countries of the world to make greenhouse gas inventories and taking actions toward reducing of CO_2 concentration buildup in the atmosphere. The protocol envisaged 5.2% reduction in CO_2 equivalent emissions on average above the 1990 level of global emissions during the first commitment period 2008–2012. However, it soon became apparent that this was not becoming successful and the emissions and the temperature continued to rise. Trends in annual as well as decadal temperature anomalies on earth (1850–2010) are depicted in Fig. 3.

India has 17% of the world populations. With the population of 1.21 billion (http://www.censusindia.gov.in) growing at 1.58% per annum, India is fourth largest emitter of greenhouse gases in 2015 measured in terms of CO_2 equivalent. On per capita basis India's contribution continues to be much lower than the world average and is 1.7 tCO_2/capita. As third largest producer of coal and fourth largest greenhouse gas (GHG) emitter, its total emissions are only 6% of global emissions. India's greenhouse gas inventory from various sectors is shown in Fig. 4.

In the Post Kyoto phase of climate agreements, the Paris Agreement of CoP 21 (21st meeting of Conference of Parties) held in 2015 under UNFCCC has Intended Nationally Determined Contributions (INDCs) as goals set to be achieved by 2030. India's intended NDCs aimed at propagation of healthy, green, and sustainable path to economic development included (i) to reduce the emission intensity of its GDP by 33–35% by 2030 from 2005 level, (ii) To achieve 40% cumulative electric power installed capacity from nonfossil fuel resources by 2030, (iii) To create an additional carbon sink of 2.5–3 billion tons of CO_2 equivalent through additional forest and tree cover.

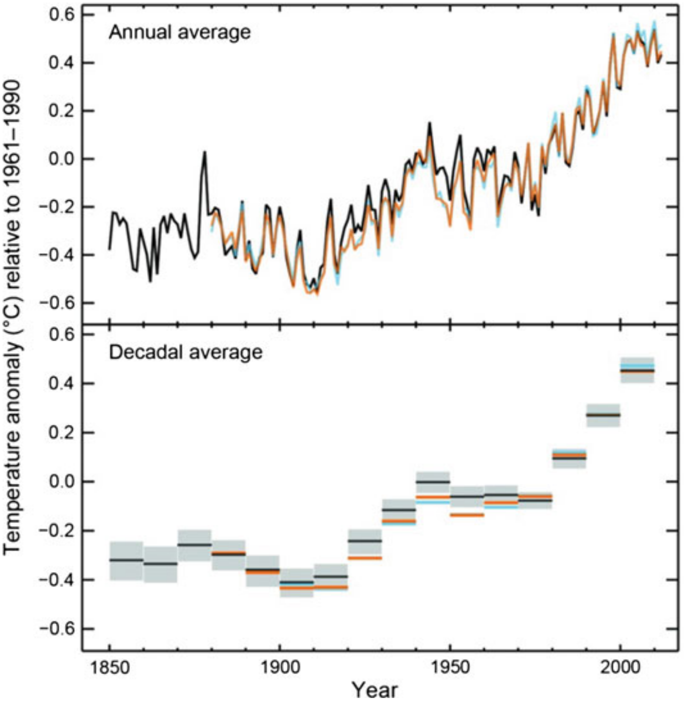
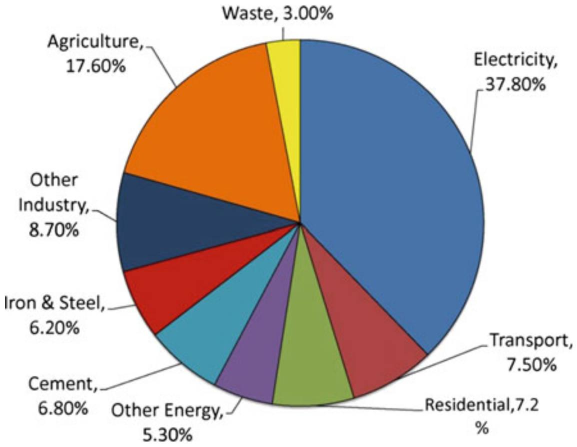


Fig. 3 Observed average combined land and ocean surface temperature anomaly (1850–2012) (*Source* IPCC-AR5 Working Group 1—Climate Change 2013: The Physical Science Basis)

Fig. 4 India greenhouse gas inventory, 2007



India has launched world’s biggest program of renewable energy development targeted at 175 GW installed capacity by 2022; of this 100 GW is expected to come from solar energy. With 30% of the population yet to get grid supply in India, total electricity installed capacity in excess of 300 GW (in July 2016) has a major share of coal-based installed capacity (60.2%) which is expected to continue as dominant energy resource for power in the next two to three decades. Indian heavy industry is also majorly dependent on coal. Reduction of GHG emissions in metal industry has been attempted through support to technology development (Goel 1997, 2008a, 2009a). To make coal-based energy sustainable so that all our energy sources are greener and cleaner, CO_2 sequestration from the energy generation and demand industry assume importance as a low carbon growth strategy (Goel 2010a). Before we discuss CO_2 sequestration choices and capacity building needs, let us look at various other geo-engineering solutions to mitigate the impact of carbon dioxide emissions in the atmosphere.

2 Part 1: Geo-engineering Approaches

Geo-engineering approaches through 'carbon dioxide removal' and 'management of solar radiation' fall into three broad categories (i) Atmospheric Engineering, (ii) Ocean Engineering, and (iii) Land Engineering.

2.1 Atmospheric Engineering

For management of solar radiation Atmospheric engineering is approached in two ways.

Aerosol Cooling—Volcanic eruptions provide a natural example of Aerosols cooling. A simulation experiment of injection of sulfate aerosols in the stratosphere suggests (Robock et al. 2008) that using one terra gram sulfur per year at a height of 25 km in the sky over Tropical belt (10°N–10°S) would be suffice to cancel the effect of global warming caused by doubling of CO_2 in the atmosphere (Crutzen 2006). A Geo-engineering model Inter-comparison Project (GeoMIP) was designed to develop global circulation model scenario. Four scenario—two for CO_2 and two for sulfate molecules (Jarvis and Leedal 2012) however indicated an inconclusive result in controlling global temperature. Besides this and ethnical as well as governance issues in this approach, an additional risk involved is of acid rain and the technique has proved to be unattractive.

Mounting Mirrors in the Sky— The other optimistic approach is proposed to place giant mirrors in the earth's orbit in order to deflect sunlight back to space. By obscuring solar radiation reaching the earth, the effect of global warming can be expected to reduce. But this too is a highly controversial approach as it can actually pose several new threats to the earth. Solar radiation management through manipulation of radiation in such a way that infrared radiation increases toward space, has also been suggested (Ming et al. 2014). Mechanics of managing global solar radiation is still a challenging task.

The atmospheric engineering third option is to remove carbon dioxide from the atmosphere by sucking of CO_2 from air, as discussed below.

CO_2 Air Capture—A scientific approach for sucking of CO_2 from air is based on use of a solid sorbent in the form of an anionic exchange residue. It absorbs CO_2 when dry and releases it when exposed to moisture (Lackner 2009). The free energy penalty of concentrated CO_2 to 1 bar is approximately 120 kJ/mol. It allows capture of emissions emanating from all types of sources, is cost-effective and a carbon negative solution. It would be possible to sequester more CO_2 then generated. It can perhaps compensate for carbon dioxide emissions from both stationary and mobile sources. A Global Thermostat designed to use heat as energy for removing CO_2 from air is considered as most innovative among the technologies for CO_2 removal and a business proposition. The captured CO_2 can be utilized into various applications such as producing a zero carbon diesel fuel by its conversion at high temperature and under pressure. Hydrogen produced from water splitting using solar energy is utilized in the process.

2.2 *Ocean Engineering*

Oceans cover 70% area of earth surface and have a vital role in climate control. They are storehouse of carbon dioxide as source as well as act as CO_2 sink. The approaches to CO_2 sequestration are through injection for storage or fertilization, as follows.

Injection of CO_2—From its point sources, captured CO_2 can be injected into sea water at different depths for storage. CO_2 injected at a depth of more than 3 km in liquid form, being denser than sea water, can possibly confine it to form a permanent lake (House et al. 2006). Less deep injection presents a potential sink for large amount of CO_2. In due course it may however, result in changing pH of sea water and disturb marine ecosystem. Depth of thermocline plays an important role in diffusion of CO_2 seepage. At further shallower depths CO_2 dispersal would however, release it back to the atmosphere through surface plumes, so not recommended. Although ocean storage potential of CO_2 has been estimated high, the excess CO_2 in the ocean waters continues to face the risk not only from leakage but also oceans becoming acidic and its adverse effects on marine life.

Ocean Fertilization—Ocean fertilization is attempted in the iron rich regions of the oceans, where carbon absorption is seen to be two to three times more as compared to other areas. Experiments using artificially added iron filings on the upper surface of oceans, to catalyze production of phytoplankton bloom as well as generate marine food, have been suggested to test the efficacy (Blain et al. 2007). It is seen that in Southern Ocean efficiency of fertilization, defined as ratio of carbon export to the amount of iron supplied, was considerably higher. However, the large-scale experiments are seen to affect ocean chemistry in other regions and have met with little success.

2.3 Land Engineering

The land engineering approach is to capture CO_2 from its point sources as also described in carbon capture, storage, and utilization (CCSU) for climate control. It requires capturing carbon dioxide from its point source, and its underground storage away from the atmosphere so that it is not released back, or its utilization into production of other chemicals for value addition. It comprises of both carbon dioxide removal (CDR) and carbon dioxide utilization (CDU). While dynamics of atmosphere and oceans prevents us to manage the engineering solutions on large-scale and in the long-term, the land processes varying on the scale of hundreds of years could be relatively more stable. In the following sections of Part 1, we present an overview of CDR and CDU options.

3 Carbon Dioxide Removal (CDR) Processes

Carbon dioxide removal (CDR) also understood as carbon capture and storage (CCS) is the most developed technique, yet in demonstration stage. It comprises of various technology sub-components as below.

3.1 Capturing CO_2

In the discussions so far CO_2 capturing processes are not elaborated. Land engineering approach of CCS originated with the idea of capturing CO_2 from its point sources which include fossil fuel-based power plant or an industrial outfit. The flue gas comprised of several impurities as well as gases including CO_2. The CO_2 capture modes have been suggested for pre- combustion, during combustion, and post combustion flue gas. In each of these CO_2 separation technology choices are based on the temperature and pressure of the flue gas. Capture technologies are categorized as; chemical absorption, adsorption, membrane separation, cryogenic separation, and hydrate making processes. Application of various gas separation technologies for CO_2 in a power plant can have a share of up to 70% in the total cost of CCS technologies. Significant research and development efforts are therefore required to make them cost-effective and reduce energy penalty.

Individually, there are challenges to be met in each of the process technology. In *absorption* amine-based process there is significant solvent loss, corrosion problems, and generation of volatile compounds. Alternatives such as use of ionic liquids (ILs), ammonia as absorber, and chilled ammonia process for CO_2 capture are also being investigated. A large number of studies have been reported in CO_2-ILs systems. Ways to develop molecular design of ionic liquids for CO_2 capture as most promising solvents at ambient temperature have been carried out (Zhang et al. 2008).

The ammonia process is also considered energy efficient as it makes use of waste heat and is also free from corrosion and toxicity (Kozak et al. 2009). However, large-scale applications of these are needed to be pursued. In *adsorption* use of liquid or solid adsorbents such as zeolites, activated carbon, hydrotalcites, and others, to bind CO_2 on their surface is made. Pressure Swing Adsorption (PSA) helps in recovery of the adsorbent. The process has lower energy penalty than the absorption process, but there are other economic considerations. Use of industrial and agriculture-based residue sorbents for CO_2 capture require attention to reduce the cost of capture significantly (Olivares–Marin and Maroto–Valer 2012).

Thin *membranes* can be used as filters for separation of CO_2 in the flue gas. In this process using polymeric, ceramic, and metallic membranes; 80–88% CO_2 efficiencies are achievable (Audus 2000). However, in its large-scale application to flue gas in power plants much remains to be done. Alternatively, *cryogenic distillation* of flue gas can help in solidifying CO_2 at—135 °C, which is then compressed to 100–200 bars. The process is quite energy intensive and has not been practiced. However, presently its application to oxyfuel combustion flue gas is being tested with renewed interest (Tuinier et al. 2010). CO_2 separation using *Hydrates* is another option. It exposes flue gas from a power plant to water stream under high pressure. The CO_2 gets caged in the lattice of water molecules. From hydrates so formed it can be separated. By improving hydrate formation rate and reducing the water pressure, better CO_2 capture efficiency can be achieved. The advantage is that energy penalty is low. The technology is in R&D phase (Leung et al. 2014).

The capture technology is not only cost intensive, but is also materials intensive and involves higher energy penalty. Second generation and transformational technologies are being developed to make it cost-effective. Three pronged research is focused on (i) new materials, (ii) new processes, and (iii) compact equipment design. It is expected that the second generation capture technologies would become available for demonstration in 2025 and may result in 20% reduction in the electricity cost, while the transformational technologies would reduce it to 30% in a 2030 timeframe (GCCSI 2015).

3.2 CO_2 Underground Storage

To cage CO_2 in natural underground surroundings has taken shape as a means to permanently storing it. The CO_2 is injected in the supercritical phase, which is attained at the temperature of 304.1 K and pressure of 73.8 bars. Injection of CO_2 into deep saline aquifers, oil & gas fields, un-mineable coal seams, shale, and basalt rocks has been studied (Bachu 2000). CO_2 geological reservoirs like saline aquifers require appropriate porosity, thickness, and permeability of the reservoir with a cap rock with good sealing capability (Solomon et al. 2008). Inter-Governmental Panel on Climate Change (IPCC) study has indicated that geological formations have capacity of 2000 gigatonnes (Gt) of likely CO_2 storage; which included 1000–10,000 Gt in saline formations, 675–900 Gt in oil and gas fields, and 3–200 Gts in coal beds worldwide (IEA 2004). CO_2 storage potential of deep saline aquifers is the highest. The parameters affecting mineral and geochemical trapping in aquifers have been investigated.

Globally, a large number of infrastructural projects are in various stages of operation, planning, and conceptualization to test efficacy of storage of captured CO_2. World's first commercial CO_2 storage project Sleipner was started in Norway in 1996. The CO_2 removed from the produced hydrocarbons at an offshore platform was pumped into Sleipner West saline aquifer inside the ocean. About 15.5 million tons of CO_2 has been injected until June 2015 (https://sequestration.mit.edu/tools/projects/sleipner). There is no evidence of CO_2 leakage and the CO_2 remains in situ. Most recent success story of CO_2 storage in basalts through mineralization has been demonstrated in *Carb Fix* project of Reykjavik Energy. In this CO_2 charged waters were injected as a natural analog into permeable basalt formations. The project aimed to study feasibility of permanent storage of CO_2 captured from Hellisheidi Geothermal power plant flue gas in Iceland (Sigurrdardottir et al. 2010) began in 2013. The calcite mineral formations have been reported on June 9, 2016 (Page 2016).

Boundary Dam started in 2013, became the world's first power project with post combustion CO_2 capture after the withdrawl of support to FutureGen by the federal government, USA, the first CCS project launched in 2007. Planned projects to start operation in the power sector include; CO_2 injection in Gorgon saline aquifer in Australia, Uthamanyah CO_2-EOR Project in Saudi Arabia, Pioneer and Quest saline aquifers storage projects in Alberta, Canada among others. In energy demand industry there have been a few demonstration projects for CO_2 capture. First project began in steel industry in a DRI-based plant in Abu Dhabi where 0.8 Mtpa (million tons per annum) CO_2 capture is planned for the purpose of EOR. Illinois Industrial Bio-CCS, Kemper County clean coal energy facility, and Petronova carbon capture are other CCS projects in the pipeline (GCCSI 2015). Nonetheless underground storage of CO_2 is not only expensive, but continues to face issues of permanency, project boundary, leakage, safety, and many other unresolved challenges including legal/regulatory in several countries, making it desirable to explore CO_2 utilization options.

4 Carbon Dioxide Utilization (CDU) Technologies

4.1 Definition and Motivation

> CO_2 conversion and utilization research is important and should be an integral part of research and development for carbon management and sustainable development.
>
> —C. Song, Pennsylvania State University (2006)

Carbon Dioxide Utilization (CDU) also understood as carbon capture and utilization (CCU) refers to reuse of carbon dioxide emitted from power or industrial plants into value added products. It involves CO_2 captured from its point sources and its utilization through chemicals and biological means as well as injection underground for fuel synergy such as Enhanced Oil Recovery (EOR) and Enhanced coal bed methane recovery (ECBM). Several important reviews on carbon dioxide utilization (CDU or CCU) have dealt with the technical, economic, and strategic issues (Kikuchi 2003; Song 2006; Aresta and Dibenedentto 2007). As such the process of utilization of CO_2 in chemical industry has been known for more than a century. CCU technologies in the current context of rising global temperature are being tried now. They are advancing rapidly with research trends intensified toward developing engineering options for the energy industry (Huang and Tan 2014). Eventually with the replacement of fossil fuels by renewable energy supply, chemical utilization can become sustainable. The option of CO_2 utilization is through EOR by injection of captured CO_2 in depleted oil fields. It can lead to a recovery of oil up to 5–20% of the total original oil in place (NETL 2010). Using natural CO_2 EOR has been a commercially viable option, while from the use of anthropogenic CO_2 it is in demonstration stage.

Economic synergy and resource conservation are main stimulus in CO_2 utilization technologies described as (i) Indirect or CO_2 conversion and (ii) Direct or CO_2 nonconversion.

4.2 CO_2 Indirect Utilization

Many possibilities exist for CO_2 indirect utilization by using chemical, biochemical, and biotechnological means. Value added products such as energy fuels, polymers, and carbonates can be produced from its chemical conversion. It is predicted that worldwide capacity of chemical utilization could be up to 1 Gt of CO_2 per year (Song 2006) although current use of captured CO_2 is less than 2% of the total emissions. Being chemically inert, use of catalyst, application of high temperature, and/or pressure and/or copolymerization with either organic compounds (Huang and Tan 2014) are required to activate the reaction with CO_2. There are many scientific and technical challenges in development of novel materials for CO_2 capture and for catalyst. Reaction with more reactive compounds can be enhanced to create C–C, C–N, and C–O bonds and afford new compounds.

Catalysis is used in production of almost 25% of all chemicals. In a catalytic process of CO_2 conversion the main hindrance is requirement of huge amount of catalyst (Aresta and Dibenedetto 2007). To avoid use of catalyst and achieve high efficiency in chemical activity plasma arc techniques have been applied (Tao et al. 2011). However, the huge energy demand for reaching the plasma stage has been the main hindrance in this approach. Use of nano-catalysts can be more efficient for CO_2 conversion into methane and methanol (Tan et al. 2012). Use of heterogeneous catalysts for copolymerization of CO_2 with epoxides in presence of yttrium-based catalysts (Dai et al. 2009; Razali et al. 2012) is being researched to produce polycarbonate silica nano-composites.

Technique of microalgae absorption of CO_2 leads to biomass which can produce lipids, proteins, and carbohydrates, and it can be utilized further to produce biofuels, or food or pharmaceuticals by trans-esterification process. 1.8 t of CO_2 can be fixed via cultivation of 1.0 t microalgae (Fernandez et al. 2012; Farelly et al. 2013). Management of pH during cultivation is critical for the growth of microalgae. Study of carbon concentrating mechanisms in photoautotrophic organisms and nonphotosynthetic organisms can potentially lead to the development of cost-effective methods of CO_2 sequestration (Puri and Satyanarayana 2010). Controlled micro organism activation methods using photo-bioreactors are under development.

The CO_2 utilization for production of energy fuels is most attractive biochemically as well as chemically, as these can replace fossil fuels to some extent. Methanol can replace gasoline in automobiles to reduce CO_2 emissions and it is feedstock for Dimethyl Ether (DME), which is a derivative of methanol produced from distillation of by-products under high pressure methanol synthesis. The conversion of CO_2 into methanol, though was known since 1977, it requires to replace CO with anthropogenic CO_2 in its synthesis from syngas using metal-based catalysts (Ganesh 2011), which means a higher reaction temperature (Song 2006; Pojanavaraphan et al. 2013). A facility for CO_2 utilization from a geothermal power plant in Reykzank, Iceland has been established to make methanol for use in vehicles. The concentration of CO_2 is about 90% in the flue gas. The plant is named as ‘The George Olay Renewable Methanol Plant’ in the honor of Nobel Prize Winner Prof George Olah, who advocated ‘Methanol Economy’. Conversion of CO_2 into polycarbonates and plastics has also attracted attention of the energy industry into marketable production (Ofélia de Queiroz et al. 2014). CO_2 can be utilized for synthesis of Dimethyl carbonate (DMC) which is biodegradable and nontoxic chemical (Mbuyi et al. 2012). DMC is a replacement of toxic and hazardous phosgene in the synthesis of polycarbonates.

The CO_2 can also be utilized to in situ mineralization with mafic and ultra-mafic rocks or with inorganic waste from mining or metal industry (Elenova et al. 2012). Carbonation reaction takes place in contact with metal oxides, also in direct or indirect processes. In the direct process carbonate precipitation occurs in a single step under high pressure (Metz et al. 2005).

CO_2 reacts with MO_x in a reaction as follows

$$MO + CO_2 \rightarrow MCO_3 + \text{heat} \tag{1}$$

Here M is metal like calcium, magnesium, or iron.

Indirect process is a multi-step process, in which metal is separated from mineral matrix; metal is then changed to hydroxide state in a hydration reaction, which reacts with carbon dioxide to form a carbonate. In CO_2 utilization industrial slag from a plant can be carbonated when olivines are present. In a chemical processing plant after mining, the waste containing silicate rocks can also help in CO_2 conversion. The equations are;

$$M(OH)_x + HCl \rightarrow MCl_2 + H_2O \tag{2}$$

$$MCl_2.H_2O \rightarrow M(OH)_2 + Cl_2 \tag{3}$$

$$M(OH)_2 + CO_2 \rightarrow MCO_3 + H_2O \tag{4}$$

Metal oxides occurring inside geological formations react on geological time scales and it is known as silicate weathering. Mineral carbonation has several advantages over other chemical conversion as (i) it does not require pure stream of CO_2, and the flue gas can be used directly, (ii) carbonate formed is quite stable, with low risk of CO_2 leakage, and (iii) energy requirement is comparatively less.

4.3 CO_2 Direct Utilization

Direct or nonconversion CO_2 utilization option is based on injection of CO_2 in depleted oil fields and abandoned coal mines for enhanced oil recovery and coal bed methane recovery, respectively. Enhanced oil recovery using CO_2 has been successfully operated as tertiary recovery method in depleted oil fields especially in USA and Canada since almost 40 years. CO_2-EOR is commercially viable option at present and can enhance oil production by recovery of up to 5–20% of total original oil (NETL 2010), but the use of captured CO_2 from power plants for EOR is under demonstration. In this some of the challenges are; simulation of CO_2 migration inside the reservoir, geochemical modeling, 3D seismic, and leakage assessment, etc., (Leung et al. 2014). In coal beds studies on CO_2 injection and release for trapped methane have been successfully carried out in USA, Canada, China, Japan, and Australia during 1990 and early 2000 (Kelafant et al. 1992; Günter 2000). Enhanced coal bed methane recovery relies on the mixing and greater affinity of CO_2 molecule with coal and release of methane molecule from the coal seams and provides clean gaseous fuel for energy, not yet commercial.

Important CO_2 utilization global R&D projects are; (i) CO_2 Chem in UK for reuse as a single carbon chemical feedstock for producing value added products and processes is a network of 800 global members from 300 different organizations, (ii) 4CU—Comprehensive and Coordinated approach for Carbon Capture and Utilization, (iii) Program of the UK Centre for Carbon Dioxide Utilization (*CDUUK*). (iv) *SCOT*—Smart CO_2 Transformation project is vision for Europe, (v) *EnCO$_2$re*—Enabling CO_2 reutilization a European Institute of Innovation & Technology project, (vi) *Carbon Utilization* launched by National Energy Technology Laboratory, USA to achieve successful implementation of various industry applications in different time horizons. Its four main research focus areas are; cement curing, polycarbonate plastics, mineralization, and additional hydrocarbons recovery. With the introduction of carbon capture and utilization legislation in U.S. Senate in July 2016, adoption of carbon utilization by industry is expected to grow.

4.4 Current CO_2 Applications for the Energy Industry

The CO_2 has many well-known uses in variety of products where properties of inert gas are desirable. Its common uses are in food processing industry as carbonation, food packing, and wine production, etc., or in fire extinguishers where high purity CO_2 is used. These applications would however not be profitable for captured CO_2 from the flue gas. Vital technological applications of energy industry flue gas are as supercritical solvent, in pharmaceuticals & urea production, waste water treatment, concrete curing, and waste utilization in metal industry among others. Studies have been carried out to develop strategies to reduce GHG emissions from fossil fuel use in steel industry and technology options to reduce emissions from Aluminum industry in India (Goel 2010a, 2011). The emerging conversion and nonconversion uses in the energy industry with their time frame to commercialize are listed in Table 1 .

4.5 Thermodynamic Considerations of CCU and CCS

Thermodynamic aspects of CO_2 conversion and removal processes play an important role in the applications. From Life Cycle Analysis (LCA) and cost analysis of CO_2 abatement into useful products through chemical conversion, the IPCC reports in 2005 noted that 'scale of captured CO_2 in industrial process is too small, the storage time too short and the energy balance too unfavorable for industrial uses of CO_2 to become significant as a means of mitigating, climates change.' Since then several LCA studies have been carried out to determine environmental impact of carbon dioxide capture and utilization (CCU) vis-a-vis carbon dioxide capture and storage (CCS) (Metz et al. 2005; Brentner et al. 2011). CO_2 chemical conversion processes are largely endothermic. The overall impact is a factor of power plant technology, CO_2 separation process, and storage or utilization option.

Further scientific investigations have led to more insightful conclusions. Singh et al. (2011), Cuellar–France and Azapagic (2015) have indicated that global warming potential (GWP) is sensitive to CO_2 capture methods and utilization options as well as whether flue gas is used directly or purified CO_2 is used. Utilizing CO_2 from power plants for enhanced oil recovery increases GWP as compared to CCS. Using pure CO_2 captured in MEA process also increases its GWP by 30–60% (Hertwich 2008). For cultivation of microalgae in an open raceway pond, the GWP is much higher in comparison to in a flat plate bioreactor (Styring et al. 2011), which is more efficient. A comparison of environment impact of CO_2 storage and CO_2 utilization technologies show that average global warming potential in CCS studies is estimated at 276 kg CO_2 sq./tCO_2 removed. The GWP of CCU option is 216 times higher than CCS (59.4 tCO_2 sq./tCO_2). However, carbon mineralization and EOR can have much lower GWP 2.9 and 1.8 times than CCS, respectively, (Cuellar-France and Azapagic 2015). Greatest GWP reduction (82%) can be achieved in Oxyfuel combustion and IGCC plants (Stephenson et al. 2010).

Table 1 CCU technology in energy industry—current and emerging applications and time to commercialize

Technology application	Description	Industry	Potential and permanence	Time to commercialization
CO_2 INDIRECT UTILIZATION				
Carbon mineralization	CO_2 reacts with mineral or industrial waste products, forming Metal Organic Frameworks. Resulting new composites can be used in construction and contribute to reduction of CO_2 emissions	Minerals	>300 Mt/year permanent	1–5 years
Concrete curing	Waste CO_2 fuel gas stream used to cure precast concrete. CO_2 is stored as a nonreactive limestone within the concrete. Reduces need for heat and CO_2 emission of precast concrete	Cement	30–300 Mt/year permanent	Already operating on commercial scale
Bauxite residue carbonation	CO_2 reduces alkalinity of slurry from aluminum industry, which can be used as a soil amendment and reclamation of aluminum mines	Aluminum	5–30 Mt/year permanent	Already operating on commercial scale
Algae cultivation	Microalgae absorb CO_2 and then get converted into proteins, fertilizers, and biomass for biofuels	Energy	300 Mt/year nonpermanent	1–5 years
Liquid fuels-methanol	CO_2 and hydrogen catalytically are converted to methanol at moderate temperature and pressure, which can then be blended with gasoline. Hydrogen used in the reaction is produced from electrolysis of water	Transport	>300 Mt/year nonpermanent	1–5 years
Liquid fuels-formic acid	CO_2 electro-reduced in water to produce formic acid, which is used as a hydrogen carrier	Energy	>300 Mt/year nonpermanent	5–10 years
Polymers/Chemical feedstock	CO_2 transformed into polycarbonates using zinc-based catalyst	Polymer	5–30 Mt/year nonpermanent	1–5 years
Basic oxygen furnace	CO_2 is used as bottom stirring agent in basic oxygen furnace	Steel	<1 Mt/year	–
Pulp washing operation	CO_2 is used to reduce pH during pulp washing	Paper & Pulp	<1 Mt/year	–

(continued)

Table 1 (continued)

Technology application	Description	Industry	Potential and permanence	Time to commercialization
Water treatment	CO_2 is used for demineralization of water after reverse osmosis	Water Purification	<5 Mt/year	–
Chemical systems	A wide range of chemicals with C and O as elements can utilize CO_2 as feedstock. In this process acetic acid, alcohols, ester, and sugar, etc., can be produced	Chemicals	<5 Mt/year	–
Urea yield boosting	Ammonia reformer flue gas of a fertilizer plant and Ammonia and CO_2 to convert to Urea and produce additional fertilizer	Fertilizers	5–30 Mt/year nonpermanent	Already operating on commercial scale
CO_2 DIRECT UTILIZATION				
Desalination	CO_2 mixed with brine at high pressure and temperature to form hydrates that can be removed to produce clean water	Water Purification	30–300 Mt/year nonpermanent	5–10 years
Enhanced oil recovery	CO_2 injected into a depleted oil well to increase pressure and reduce the viscosity of the oil, increase the amount of oil that can be recovered	Oil & Gas	30–300 Mt/year permanent	Already operating on commercial scale
Enhanced geothermal systems	CO_2 in supercritical form transfer's geothermal heat as a heat exchanger fluid. It can generate power directly as working fluid in a supercritical CO_2 turbine	Renewable Energy	5–30 Mt/year permanent	5–10 years
Enhanced coal bed methane	CO_2 injected into partially depleted coal seams displacing and releasing adsorbed methane to the surface for it to be captured and consumed as fuel. Power plant fuel gas can be used directly	Coal & Energy	30–300 Mt/year permanent	1–5 years
Super critical CO_2 as solvent	Supercritical CO_2 because of low critical temperature and moderate pressure requirements can be used as a solvent to isolate targeted entity	Pharma Industry	<1 Mt/year	–

Source Adapted from 'Accelerating the uptake of CCS: industrial use of captured carbon dioxide' (http://status.globalccsinsitute.com) and Pembina Institute Report, Canada (https://www.pembina.org)

These results are indicative only and further studies of environmental impacts other than GWP and economic viability are being made. Utilization of waste CO_2 into industrially useful chemicals and energy fuels is one of the rapidly growing fields of research (Ampelli et al. 2015) getting acceptance from scientific community as technology for mitigating climate change, thus providing energy security for coal-based economies. Hung and Tan (2014) have observed that 'global strategies of CO_2 mitigation should focus on utilization of CO_2 … for the environmentally benign processes, the production of industrially useful chemicals from CO_2 and the CO_2 recycling combined with renewable energy to conserve carbon resources.'

For CO_2 management in the energy industry, UNIDO—World Bank—GCCSI Global Technology Road map having a focus on energy intensive industries identifies five main sectors as; high purity CO_2 sources, iron & steel, cement, refineries, and biomass-based sources toward a low carbon growth strategy. The roadmap addresses cross-cutting issues and long-term vision up to 2050.

The four classical feedstocks of chemical industry namely; petroleum products, natural gas, coal, and biomass make 40 basic chemicals, which are the source of 400 intermediate chemicals and lead to as many as 40,000 chemicals (Araújo et al. 2014). In the industry value chain CO_2 has been optimistically suggested as *5th classical feedstock,* adding to the list of four. Conversion of CO_2 into plastics would not only reduce the dependence on petroleum resources and conserve materials resources, but would also have potential to become environmentally safe and economically viable with emerging applications. Already a few pilot and commercial scale plants for CO_2 utilization have been built for production of polycarbonates, polyurethanes, urea as well as monoethylene glycol (MEG)—a precursor to polyester fibers. More research however, is needed in CO_2 utilization to study wide range of energy, economic and other environmental impacts, taking into account the power plant efficiencies and way to capture CO_2. Policy instruments towards development of peripheral technologies, such as hydrogen production and use of renewable energy deployment for CO_2 recycling in industry are critical elements for the success of CO_2 conversion and are also to be addressed.

5 Part 2: Need for Capacity Development

By definition capacity development is 'the ability creation to perform desired functions and solve problems in a specific topic.' In the case of CCS, geo-engineering approach is required and one can define capacity development in several ways. It could mean underground storage capacity building in different countries. It could be in the form of knowledge sharing and technical capacity building for establishment of research capabilities in storage. It could also mean exposure of management boards and policy makers for motivating them to acquisition of technology. It could be developing national capabilities, in view of the global advancements and capacity development taking place. Sometimes it is required to simply have a mechanism to incentivize the adoption of technology. The carbon capture, storage and utilization (CCSU) technology is a multi-disciplinary scientific and engineering subject, therefore basic understanding of various scientific topics as well as their economic and environmental implications in the global context is needed through capacity building. Intergovernmental Panel on Climate Change (IPCC) has commented on wide spread applications of CCS (U is silent in this), which would depend on technical maturity, the cost of technology and its overall potential, as well as the need for diffusion and deployment. There have been extensive capacity development efforts to apply the technology, knowledge sharing on development of scientific knowledge, skills and regulatory aspects, and public perception.

5.1 International Initiatives

Although research programs were undertaken in USA, Japan, and other countries to develop scientific methods of CO_2 sequestration early, internationally the efforts in capacity building in CCS formally began around 2003. Asia Pacific Economic Corporation (APEC) was first to initiate a three phase capacity building project in APEC region countries to explore potential for geological CO_2 capture and storage technology with the objectives of enhancing the capacity of APEC developing economies to undertake CCS projects and build awareness, knowledge and skills for their implementation. The major initiative came from Carbon Sequestration Leadership Forum (CSLF) of Department of Energy, USA which also began in 2003. The CSLF formed a Capacity Building for Emerging Economies Task Force (CBTF) in 2005 and began a series of capacity building workshops focusing on awareness raising and participatory dialogue.

Under the umbrella of CSLF Task Force first Capacity Building in Emerging Economies was held as Round Table Discussion in Pittsburg, USA in 2007 in conjunction with the 6th Annual Conference on Carbon Capture and Sequestration participated by Indian researchers and policy makers. Initially these were held in conjunction with its Technical Group meetings. The CSLF having 23 countries as its members formally approved a Capacity Building Program in 2009 with the object to develop knowledge tools, expertise, and institutions. A Capacity Development Fund (CDF) has been established in 2011 with a projection of nine capacity building projects in its five developing member countries. Developing country member countries are expected to participate in these to gain knowledge about global CCS implementation.

Need for CCS training continues to grow as it was pointed out that there are not sufficient capacity and resources in developing countries and emerging economies (Bachu 2009). Key modes for capacity building in CCS were suggested as; (a) information dissemination, (b) undergraduate studies, (c) postgraduate research, (d) professional training programs (Beck and Gale 2009). World Bank (Zechter 2013), UN Industrial Development Organization (UNIDO), Asian Development

Bank (ADB), and other multi-lateral organizations have been instrumental in funding awareness raising capacity building programs, while commissioning specific studies on CCS in a number of developing countries with the object of identifying pilot projects. A CCS Trust Fund has been created. In Egypt and South Africa studies reported on assessment of CCS potential so as to identify pilot projects and ascertain barriers in implementation (Kulichenka and Ereina 2012).

Within the global framework, CCS has been hot topic in Subsidiary Body for Scientific and Technological Advice (SBSTA) holding workshops since 2006 (Bill 2006; Goel 2006) as well as International Schools in Geophysics held at Ettore Majorana, Sicily, Italy. In Europe trainings have been held on CO_2 storage through Summer schools and as specific modules under International programs such as Network of Excellence in Geological Storage of CO_2 (CO_2GeoNet) (Fouillac et al. 2008). European Union (EU) CO_2ReMoVe involving twenty nine partners across Europe launched the courses toward regulations in the area of monitoring and verification of CCS. These courses have largely catered to capacity building among European Union member countries. The CO2CRC is another leadership education program in Australia for preparing the community, industry, and government for CCS deployment.

The Global Carbon Capture and Storage Institute (GCCSI) has added another milestone by launching a target work program as Capacity Development Country-of-Focus in non-Annex I countries of UNFCCC. Global CCS Institute holds webinars aimed at regional CCS knowledge sharing initiative to support accelerated technology diffusion, improved public awareness and targeted cost reduction in future projects. In response to the need for including CCS in the formal university curriculum in Engineering and Environmental Science disciplines identified. Several universities in UK (Maroto–Valer et al. 2009) and USA have begun Postgraduate level courses with the object of creating experts in the area of CCS and learning new technologies.

5.2 *Indian Initiatives*

India has already taken a first step to recognize the scope of CO_2 sequestration research and the development plans will continue to lay a balanced emphasis on economic growth and environment. On a global platform India is one among 24 developing countries that are having CCS activity, recognizing the importance of CCS for energy security, and among the portfolio of technologies for reductions of carbon emissions (GCCSI 2015). Carbon sequestration has been a hot topic of discussion in climate change negotiations of UNFCCC which take place in Conference of Parties (COPs) every year. The CCS projects in geological formations have become eligible under the clean development mechanism (CDM). Durban COP-17 held in 2011 legitimized CCS as valid technology for both developed and developing countries and established precedence-setting regulatory framework to some extent. As an outcome of Warsaw COP-19 in 2013, countries were urged to offer their Intended Nationally Determined Contributions (INDCs) for the Post Kyoto 2020 actions so that global warming temperature does not exceed 2 °C. Accordingly, India's INDCs in Paris Accord in COP 21, among others suggest that India plans to create additional sinks for 2.5–3 billion tons of CO_2 in 2030. CO_2 sequestration also meets the sub-targets of a number of Sustainable Development Goals (SDGs) of United Nations to be achieved in next fifteen years.

The Global CCS Institute has ranked countries in four quadrants depending on their policy support relative to the level of interest they should have and develop a *CCS Policy Indicator* (GCCSI 2015). In *CCS Policy Indicator* India is placed in third quadrant with inherent interest in upper tier and policy index in lower-mid tier (Fig. 5) along with Indonesia and Russia. Brazil, Mexico, Poland, South Africa are in upper mid tier in CCS interest and in lower-mid tier for policy index. UK, Canada, and USA are in upper tiers having introduced funding for large-scale projects and market-based incentives as well as supportive regulations for power sector and for storage. Trinidad and Tobago, Algeria, and Egypt are in lower and lower-mid tiers.

The capacity building efforts in CCS in India have been started in 2004 through scientific research initiated under the Inter-sectoral program of India's Department of Science & Technology (DST). Initially two science and technology interaction meets were held in 2004 and 2006 with stakeholder organizations namely Coal India, National Thermal Power Corporation (NTPC), ONGC, Geological Survey of India, The Energy Resource Institute (TERI), R&D Laboratories, and academic Institutions participating. Specific highlights of these workshops and an

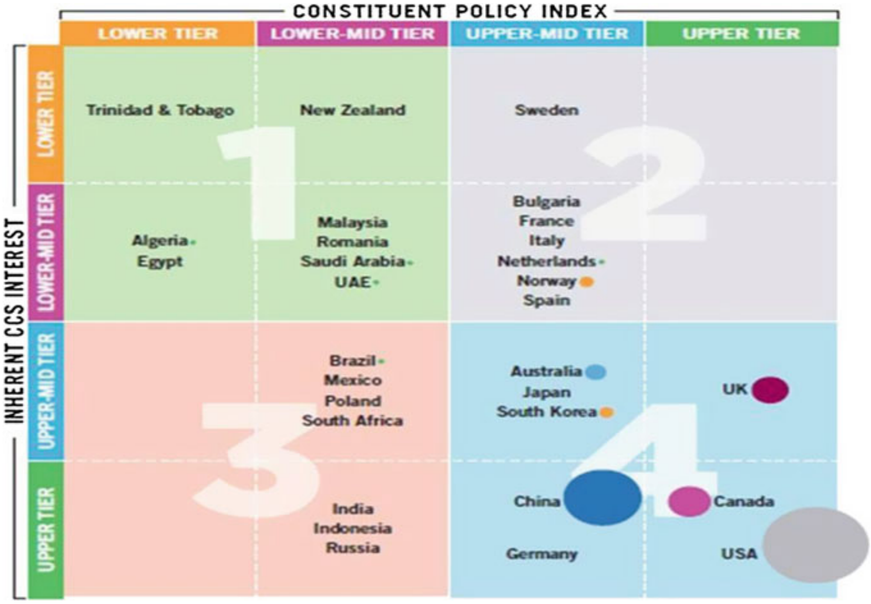


Fig. 5 The CCS policy indicator by Global CCS Institute. The *size of bubbles* denotes number of projects as on October 2015 (*Source* GCCSI 2015)

international conference held in 2007 (Kumar et al. 2007; Goel 2008b, c) led to participation of industry in scoping studies from application of CO_2 EOR in a mature oil field of Ankleshwar in Gujrat (Dimri et al. 2008), and possibility of further research on enhanced coal bed methane recovery from CO_2 storage along stratigraphic horizon of coal deposits in India. Feasibility studies of saline aquifers and basalts as future reservoirs were reported (Goel et al. 2008). In carbon capture; several CSIR laboratories got engaged in research on new materials, viz., amine functionalized materials including natural biopolymers, ionic liquids and synthesized nitrogenous activated carbon, zeolites, and alumina with further optimization in progress. Potential of PSA processes for higher CO_2 recovery from power plant flue gases and possibility of using Hydrotalcites-materials as anionic clays for CO_2 adsorption were investigated.

India's CCS policy focused on pursuing Research, Development and Demonstration and was notified as '…India will continue to participate in R&D activities and is willing to work on CCS technologies by deputing its scientists and engineers to sites in other countries where R&D into these technologies are being undertaken. We also support R&D into activities that seek to fix CO_2 convert it into productive uses.[1]' The Science & Technology initiative with Power has been the National Program on Carbon Sequestration Research way back in 2006 with major thrust areas identified. Indian CO_2 Sequestration Applied Research Network was launched. Preliminary studies of R&D challenges and policy barriers in adoption of CCS in power sector for super critical and oxy fuel coal combustion technologies (Goel 2009b, 2010b, c, d, e, f) were attempted. Need for geo-modeling research for better understanding of geo-environment in the earth processes for CCS was recommended (Goel 2012).

Concurrently, Indian Industry's initiatives for capacity building included; National Thermal Power Corporation (NTPC) workshop on Carbon Capture and Storage held in 2005, 2007 and 2011. Attended by the policy makers in power, coal and oil sectors, and academic scientists, another follow up Round Table on CCS was held in 2012 at the NTPC Power Management Institute, Noida. The NTPC has already pilot tested a project to sequester CO_2 in open pond using algal technology at its utility site in Faridabad. The Bharat Heavy Electricals Ltd. (BHEL), Trichy training workshops on CCT and CCS were held in 2011 and 2012. BHEL hosts a EU TREC—STEP CCT-CCS cluster for advancement of technologies (Kumar 2011). National Aluminum Co. (NALCO), Odisha has successfully commissioned a pilot-cum-demonstration CO_2 sequestration plant. The ONGC, Tata Steel, and Steel Authority of India (SAIL) have created carbon neutral research centers. In the Indian fertilizer sector National Fertilizer Ltd (NFL), Indian Farmers Fertilizer Cooperative Limited (IFFCO), and Nagarjuna Fertilizers and Chemicals Limited (NFCL) have adopted carbon capture technology. The captured CO_2 is said to be of

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[1] Ministry of Power office memorandum dt. 24th April 2009 (source-NTPC background paper 2011).

99% purity which will be recycled again to be used in the production of urea from ammonia.

The challenges of economics, energy penalty, and safety of CCS technology related to power generation for emission abatement are major hurdles identified toward the low carbon growth strategy. It is time to revisit the policy and create enabling environment for the industry for technology development and make planned investment in CCU research as a long-term energy security measure.

5.3 ACBCCS 2015 and Contents of the Book

The CCU research and development (R&D) is one of the means by which one can expect future growth in Carbon Science and Technology. It requires human resource development and capacity building for not only to create awareness but also for education. Young academicians need a greater exposure on India specific issues for CCSU research. Awareness and Capacity Building in Carbon Capture and Storage (ACBCCS) workshops were conceived in-house in 2009. The first two such workshops namely ACBCCS 2009 and ACBCCS 2013 covered the entire gamut of research and advances made in carbon capture, storage, and its utilization. Leading industrialists shared their experiences and the complexities involved which was an eye opener to many of the young participants. There has been a huge motivational effect on the work being carried out in various research centers and universities in the country as the participants interacted with the policy makers and were exposed to practical utilization of their research (Goel 2010c; Goel et al. 2015). Acclaimed as timely initiatives for sustaining the momentum for education and future research in the country, some Universities and National Institute of Technology in India began teaching in CCS as part of their Green Technology curriculum.

The third workshop in the ACBCCS series has been held from July 27–31, 2015 in New Delhi. The theme was CO_2 removal processes in the Energy Intensive Industry toward a low carbon growth strategy. The CO_2 Sequestration from energy industry provides a future option for dealing with increased accumulation of greenhouse gases. For it to be a viable option, it needs to be cost-effective, reliable, and safe in comparison to other carbon management options, such as improvements in energy efficiency and renewable energy sources. The ACBCCS 2015 was participated by a large number of experts in academia, industry and top research centers in the country namely; Anna University, Chennai; Manipal University, Imphal; University of Calcutta, Kolkata; Delhi University and Jawaharlal University; Maulana Azad Institute of Technology, Bhopal; Bharatidasan University, Trichy; National Thermal Power Corporation, Noida; Tata Steel, Jamshedpur; National Fertilizers Ltd. Vijaypur; Oil & Natural Gas Corporation (ONGC) Energy Center, Jawaharlal Nehru Advanced Research and Development

Center, Nagpur; ICRISAT Development Center, Andhra Pradesh; CSIR- National Geological Research Institute, Hyderabad, TamilNadu Agricultural University, Trichy and Central Mining and Fuel Research Institute, Dhanbad. Recommendations made in the workshop are two folds (Goel 2016); Creation of a CO_2 capture test facility for the research already conducted, which can benchmark and help in making the process cost-effective, and Initiation of a multi-sectoral research program for development of ammonia-based CO_2 capture with the participation from concerned sector namely Ministries of Chemicals and Fertilizers, Agriculture, Steel, and Power as well as academic institutions. The CCU being an infrastructure-intensive multi-disciplinary research, it was suggested that a nodal institution is needed to organize knowledge sharing among the various stakeholders in order to accelerate the pace of work in the country. The specific recommendations for advancement of CO_2 sequestration technology in the industry are summarized as below.

(a) A knowledge center as think tank should be set up to start a new direction for research in CO_2 capture and utilization with a number of key organizations, both from Industry and academic institutes participating in it.
(b) A knowledge sharing network (CCU-Net) among the various stakeholders should be created.
(c) The model network could be designed to support India's policy and address technology challenges of capacity building virtually in all areas of carbon capture, storage, and utilization.
(d) By interfacing with industry, academia, and policy makers such a network could help in assessment of Indian potential in CO_2 capture, compression, transportation, storage as well as utilization options toward the policy advocacy.
(e) The center should also take up inter and intra-networking to provide thrust to technology development as well as to develop standards for technology benchmarking.

5.3.1 The Book on Carbon Utilization

The aim of present book on CARBON UTILIZATION is to analyze how CO_2 re-use—chemical, biochemical, and biological processes can contribute to terrestrial utilization for industrial applications and to put forth perspectives on carbon removal and utilization options in the knowledge domain. Specific applications from the energy intensive industry are presented. The book has 19 chapters grouped into four parts as; CO_2 Emission, Sequestration and Utilization; Terrestrial Sequestration Options; Low Carbon Growth Strategy from CO_2 Utilization, and Current Research and Green Technology Perspectives from Industry.

What should be the low carbon strategy; is the key policy issue for achieving energy security for India in the context of climate change; whether to adopt CCS or not? The section one covers a policy dilemma for energy security in India. The Chap. 1 of the first section presents an overview of trends in carbon emissions, geo-engineering solutions for climate control, and carbon dioxide capture and removal processes by way of its utilization or reuse as a low carbon growth strategy. The need for capacity development and examples of international and national initiatives are cited with recommendations. Timely introduction of supercritical technology and a goal of have all new power plants to be based on supercritical cycle by 2022 and its management in power sector may significantly contribute to reduction of CO_2 emissions. This is the theme of Chap. 2. India has already set gigantic goal of achieving 175 GW of renewable energy-based electricity generation by 2022. Yet in the real terms this contribution will be approximately 45 GW equivalents to fossil fuel-based capacity in electricity generation. Chapter 3 proposes a Green Power Mission by way of clean energy technology development from renewable sources as well as coal-based generation with CCS for achieving a low carbon growth. A conceptual integration of CO_2 sequestration plant with solar thermal is presented.

After the first section on policy advocacy, the second section is about research in terrestrial sequestration options for CO_2 in the soil, forests, and coastal wet lands as well as enzymatic biomimetic carbon sequestration challenges. These are covered in Chaps. 4–8. Chapter 4 is about development of information on the spatial distribution of soil type to understand the role of soils in capturing and storing elevated atmospheric CO_2. Such data are vital for advancement of appropriate management techniques for carbon sequestration at the national level. In Chap. 5 authors further examine the soil carbon stock and soil CO_2 flux in the different terrestrial ecosystems, i.e., forest, bamboo, and grasslands of Northeast India and relate it to land use patterns. An assessment of the potential of tree growth in different altitudes and its contribution in carbon dioxide sequestration in Panchamalai Reserve forest in Tamil Nadu, India and its role in sustainable management practices are covered in Chap. 6. In the coastal zone ecosystem of Lakshadweep the observed data shows that density or biomass per unit area of the species plays a crucial role in regulating the carbon pool in the region. This is the theme of Chap. 7. A detail review of enzymatic CO_2 capture potential and current research in advancements made in the production of recombinant C, as has been provided in the Chap. 8.

In third section Chaps. 9–14 are describing CO_2 utilization as a low carbon growth strategy in India. The CO_2 separation or capture from flue gas, its storage, and the technologies to convert the separated CO_2 into usable chemicals employing methods such as, chemical, photochemical, electrochemical, and bio-processes are presented in Chap. 9. Chapter 10 provides biological solutions using a photo-bioreactor for the utilization and conversion of CO_2 from a power plant into viable economic products. A powerful tool to mitigate CO_2 is clathrate hydrates in deep sea. This novel way of sequestration of CO_2 as gas hydrates and research challenges in it are dealt in Chap. 11. Geological sequestration for enhanced oil recovery with Indian perspectives on policy is the theme of Chap. 12. The recent research results from Carb-Fix are cited. Chapter 13 covers the geologic data and scope of enhanced methane gas recovery in Indian coal fields. Experimentally determined mineralization reaction rates and kinetics should be incorporated into geochemical models to predict the permanent storage of CO_2 in unmineable deep coals after ECBM recovery. A low carbon strategy using advanced technology of oxy-combustion power cycle to synergize with enhanced coal bed methane recovery formed the topic of Chap. 14 from an American perspective.

CO_2 emissions from manufacturing processes are quite high. Energy Intensive industry has a share of almost one third of total greenhouse gas emissions. With this in view the fourth section of the book is on current research and green technology perspectives for energy industry. Chapters 15–19 present technology advancements taking place in Aluminum, Steel, and Cement industry for mitigation of greenhouse gases. Aluminum metal has been considered a part of solution for addressing climate change concerns. The aluminum industry however contributes 21.8 t CO_2/t Al produced. Carbon footprint of Aluminum industry and perspectives for carbon neutrality through R&D measures is the theme of Chap. 15. Chapter 16 explains result of a pilot plant at a National Aluminum company in India for micro-algae-based CO_2 capture to create an accelerated carbon sink. India is also fourth largest producer of steel in the world. Critical scientific inputs and strategies are needed for achieving CO_2 reduction in the iron and steel industry by technology management. In Chapter 17 emerging technology solutions for carbon reduction in steel production are dealt. Chapter 18 covers approach to mitigation of carbon emissions in cement production through application of new and alternate technology. More efficient CO_2 capture using Ammonia process should be developed indigenously so that it can be adopted by the multi-sector industry in India. This is strongly recommended with scientific details and is explained in Chap. 19.

5.3.2 New Research on Conversion of CO_2 into Electricity

New research at Cornell University, USA has shown that CO_2 from the industry exhaust gas can be directly converted to electricity. Oxygen assisted Aluminum—CO_2-based electrochemical cell has been designed (Al Sadot and Archer 2016) for power generation and is capable of generating up to 13 A-h for every gram of carbon that it captured. Aluminum is used as anode material and CO_2/O_2 gas mixture as an active material in cathode. The cell reduces O_2 at the cathode to form superoxide intermediates. The superoxide reacts chemically with CO_2 forming aluminum oxalate $(Al_2\ O_2\ O_4)_3$. Production of electrical energy takes place when the cell is galvanostatically discharged in an atmosphere of specific gases in the molar ratio of CO_2 and O_2 as (80:20). It is estimated that in an Al/80% CO_2 electrochemical cell 9.31 kg CO_2/kg Al can be captured from a flue gas system and abated, while the aluminum production processes are expected to result in 7.88 kg CO_2/kg Al. Therefore, net reduction of CO_2 emission is possible. The aluminum oxalate formed could be used to make oxalic acid which is used in several industries. The process does not require any catalyst and can prove to be a low carbon strategy.

6 Conclusions

Increasing CO_2 emissions and their accumulation in the atmosphere are giving rise to global warming and climate change. Management of CO_2 emissions through capture and utilization is becoming an important research topic in the recent years. We begin this paper with introduction to geo-engineering approach for climate change mitigation comprising of land, ocean, and atmosphere processes. These can be grouped in two categories as 'management of solar radiation' and 'removal of carbon dioxide.' Among these, the CO_2 sequestration or carbon capture and storage is most researched and considered an emerging energy technology. The carbon capture, storage and utilization (CCSU) processes, the current status of CDR and CDU technologies, and challenges in them are described. Examples of CO_2 applications for the energy industry from conversion and nonconversion processes in industry are cited. Life cycle studies, environment impact, and current state of affairs in their role in climate change mitigation need to be understood. In the industry value chain, CO_2 is being seen as 5th classical feedstock for the chemical industry. New research on direct conversion of CO_2 into electricity is briefly discussed.

The CCSU technology is a multi-disciplinary scientific and engineering topic; it requires inputs from diversified fields. Multitudes of capacity building activities for knowledge dissemination and short-term trainings in different countries have taken place in the last one-and-half decades supported by multilateral organizations. World Bank, UN Industrial Development Organization (UNIDO), Asian Development Bank (ADB), and others have been instrumental in funding awareness raising capacity building programme as well as specific studies on CCS in a number of developing countries with the object of identifying pilot projects. The CSLF and Global CCS Institute have been key players in capacity buildings and have held target oriented short-term trainings. In Europe trainings have been on CO_2 storage through Summer schools and as specific modules under International programs such as Network of Excellence in Geological Storage of CO_2 (CO_2GeoNet) and CO_2ReMoVe. These courses have largely catered to capacity building among European Union member countries. The CO2CRC in Australia is another leadership education program for preparing the community, industry, and government for CCS deployment.

Across the world the CCS has also become a part of formal education in some universities at postgraduate and research levels. India made a beginning in 2004 by organizing stakeholders' meets and capacity building workshops to encourage academia and industry participation in research and human resource development. The capacity development activities in India and the contents of the book are described here. In the context of Paris Agreement on Climate Change India's intended nationally determined target of creating additional carbon sinks of 2.5–3.0 billion tons by 2030 has been set. It is therefore pertinent that the focus is on carbon capture and utilization as a green technology through increased investment on R&D in the energy industry. It is expected that human resource requirement to address challenges of technology, economics, energy penalty, and safety related to power generation as well as to energy intensive industry toward a low carbon growth strategy would grow exponentially in a timeframe of 15 years from now. Evidently, as India gears to achieve a global presence in the green industry, institutionalizing ongoing efforts through networking to create CCU-Net would lead to tangible and intangible benefits as well as to optimum utilization of resources in the country.

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Chapter 2
Adoption and Introduction of Supercritical Technology in the Power Sector and Consequential Effects in Operation, Efficiency and Carbon Dioxide Emission in the Present Context

V.S. Verma

Abstract The paper highlights and traces the history of development of the power sector in India with special reference to the unit sizes of thermal turbo-generators which gradually increase from about 30 MW in 1947 to 660 and 800 MW at present. The initial focus has been on capacity addition to meet the demand increase. However, in the last two decades the greater stress was laid on the efficiency aspects of power generation to reduce the specific fuel consumption and consequently the CO_2 reduction. Reference has been made for adoption of CCS technology in our power stations and the pros and cons of the same have been discussed. Recommendations have been made towards the best practices for operation of the supercritical units in most optimal manner. Constructive criticism of the existing philosophical policies of the load dispatch centres has been made. Suggestions are also made to improve the situation. The action plan for climate change is referred to in connection with the strategy to adopt the supercritical technology in the overall improvement of the sector.

Keywords Indian power sector · Super critical technology · Operation · CO_2 reduction

Abbreviations

TPP	Thermal power plant
MS	Main steam
RH	Reheat
PLF	Plant load factor

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CEA	Central Electricity Authority
GHG	Green house gas
NTPC	National Thermal Power Corporation
PGCIL	Power Grid Corporation of India Limited
IPPs	Independent power producers
RPO	Renewable purchase obligation
CERC	Central Electricity Regulatory Commission
UDAY	Ujjwal DISCOM Assurance Yojana
T & D	Transmission & distribution

1 Background

The history of power development in India started since Independence when installed capacity of power generation was only 1367 MW, consisting of mainly the Hydroelectric Units of small capacity and few very small capacity coal fired units and diesel sets as well. The demand of electricity continuously increased and installed capacity also grew with installation of the thermal units in ratings of 30, 60, 82.5, 100, 110, 120, 140, 200/210 MW units. The units in ratings of 82.5, 110, 120, 140 and 200 MW were reheat units. The rest were non-reheat units. This scenario continued till the mid-seventies. The demand of electricity was still growing and the planner's attention was drawn to setting up of large capacity units commensurate with the increase of grid size 500 MW units were then conceived. The first 500 MW units were commissioned at Trombay Thermal Power Plant (TPP) of TATA Electric Co in the year 1984.

The increase in unit size was associated with corresponding increase in steam parameters (pressure and temperature) as well as efficiency of generation. Enhanced efficiency implies lesser green house gas (GHG) emissions.

The design efficiency and steam parameters associated with various unit sizes starting from 30 MW till 500 MW are indicated in Table 1.

It is pertinent to mention that most of the supercritical units which are in operation in various countries are operating either with natural gas as the fuel or

Table 1 Various unit sizes and main parameters

Unit size (MW)	Main stream pressure (kg/cm^2)	Main stream/reheat temperature (°C)	Gross design efficiency (%)
30–50	60	482	28.20
60–100	90	535	31.30
210 LMZ	130	535/535	35.63
210 KWU	150	535/535	37.04
250	150	535/535	38.3
500	169	538/538	38.6[a]

[a]The supercritical units will have heat rates better by about 2% over those of the subcritical units

Table 2 Parameters of supercritical units in operation

Power station	Size (MW)	Steam parameters	Fuel used	Year of commissioning	Efficiency (%)
Matsuura2	1000	255 bar/598 °C/596 °C	PC	1997	
Skaerbaek3	400	290 bar/580 °C/ 580 °C/580 °C	NG	1997	49
Haramachi2	1000	259 bar/604 °C/602 °C	PC	1998	
Nordjylland3	400	290 bar/580 °C/ 580 °C/580 °C	PC	1998	47
Nanaoota2	700	255 bar/597 °C/595 °C	PC	1998	
Misumi1	1000	259 bar/604 °C/602 °C	PC	1998	
Lippendorf	934	267 bar/554 °C/583 °C	Lignite	1999	42.3
Boxberg	915	267 bar/555 °C/578 °C	Lignite	2000	41.7
Tsuruga 2	700	255 bar/597 °C/595 °C	PC	2000	
Tachibanawan 2	1050	264 bar/605 °C/613 °C	PC	2001	
Avedore 2	400	300 bar/580 °C/600 °C	NG	2001	49.7
Niederaussen	975	265 bar/565 °C/600 °C	Lignite	2002	>43
Isogo 1	600	280 bar/605 °C/613 °C	PC	2002	

PC pulverised coal, *NG* natural gas

better quality of coal (Higher Calorific Value of the order of 6000/7000 kcal/kg). Very few numbers are in operation with coal of calorific value of around 3500 kcal/kg as available in India.

The supercritical technology has been adopted worldwide. These are in operation since 1950s specially in the countries like USSR, USA, Japan and others. The development of supercritical technology leads to better efficiency as well as consequential higher unit sizes of 800/1000 MW due to techno economic considerations.

The steam parameters and efficiency of some supercritical power plants in operation around the world is shown in Table 2.

The Central Electricity Authority (CEA) of India (Technical Standards for construction of Electrical Plants and Electrical lines) Regulations, 2010 published in the Gazette of INDIA dated 20 August 2010 prescribe the following guidelines for heat rate:-

1. Heat rate * (kcal/kWh) at 100% MCR with motor driven BFP	2. Heat rate * (kcal/kWh) at 100% MCR with turbine driven BFP
1810	1850

It may be noted that until the commissioning of 500 MW size units, the technology and other related aspects of operation and maintenance of TPPs with bigger unit sizes were under learning stage. Water chemistry is also one of the important subjects which was not very well understood with reference to the corrosion in the water tubes and in the flue gas ducting due to high temperature corrosion as well as sulphur contents in the coal and also maintaining the quality of steam and feed water in terms of dissolved silica, pH and oxygen. As a matter of fact, the grid size has been continuously increasing due to increasing demand for power, but the power plants were still operating at Plant Load Factors (PLFs) around 66% till eighties. This was mainly attributable to the teething problems in the newly adopted technology and increased unit sizes. The reasons were mainly boiler tube failures and other unit drippings on various protections, genuine and others.

The idea of installing large size units with supercritical parameters has been appreciated in the policy planning circles. However, the level of confidence in operation and maintenance of Subcritical units did not allow the planners to take a firm decision of going ahead with the Supercritical units in the country. In fact, way back in 1984, TATA Electric Co. was prevented to install a 500 MW unit with supercritical parameters at Trombay TPS. Higher reheat steam temperature of 568 °C was, however, adopted by them to gain advantage in turbine cycle efficiency.

The CEA set up a Committee under the Chairmanship of Member (Thermal), with the participation from National Thermal Power Corporation (NTPC), Bharat Heavy Electricals Limited (BHEL) and CEA in the year 1987 to go into the question of suitability of installing a larger unit's size with supercritical parameters and also to study the suitability of the supercritical technology adopted by Soviet Union (USSR) in their 200 MW units. A visit to USSR was also organised. The Committee in its report submitted that the grid size was adequate to sustain an outage of a 700–800 MW unit. It was also concluded that 700–800 MW boiler furnace size with Indian coal will be almost equivalent to a 1000 MW size boiler with better quality coal. The Committee, however, was of the firm view that the time was not ripe to adopt supercritical parameters in thermal units in India due to requirement of maintenance of a very high standard of water chemistry in supercritical units. The Committee recommended that one or two experimental units of 500 MW subcritical once through boiler designs must be installed to gain experience through designs of the boiler on the units. This will help in increasing the confidence level in O&M of the once through boilers. Accordingly, two units of 500 MW subcritical once through boilers were installed at Talchar Super Thermal Power Station of NTPC. The experience and feedback of operation of these units was also good.

Subsequently Govt set up another Committee under the chairmanship of Member (Thermal), CEA in 1989 to review the subject of next higher size of thermal unit to be adopted in the country with supercritical steam parameters. The cost aspects were also to be studied. This Committee concluded that a unit size varying from 660 to 800 MW could be adopted with supercritical parameters to gain advantage of efficiency with better steam parameters in these units. The statistics of availability of supercritical units vis a vis that of subcritical units around the world was also collected so as to arrive at the right conclusion in regard to availability of these units. From the data it was evident that the availability of some of the better operated units with supercritical parameters was by and large at par with subcritical units. This led to the conclusion that perhaps the time was right to adopt larger size units in the country with larger units to gain momentum in the capacity addition in the country. CEA consequently gave techno economic clearance to NTPC to install two supercritical units at their Sipat Power Station with 660 MW in the first stage. This power station was however delayed and the first unit of 660 MW with supercritical parameters was commissioned with commercial operations only recently in 2013 by Adani Power at their Mundra Power Station who became the first private developer in the country, to have installed and commissioned the 660 MW units in the country at the shortest gestation period of 36 months.

The above sequence of events was followed by many other developers and a large number of supercritical units in the country are now operating with 660 MW unit sizes. Four 800 MW units with imported coal have also been commissioned by M/s TATA Electric Company at Mundra. 800 MW unit size are the largest size operating today in the country.

The deployment of carbon capture and storage technology was however not agreed due to the following considerations:

a. Cost aspect (cost of generation may almost double)
b. The efficiency aspect (efficiency of generation would come down by 30% (12% points)
c. The plant footprint area would increase tremendously.
d. The disaster management plan was not known and addressed.

The country has however chalked out a plan of reducing the carbon dioxide emission from the thermal power sector as follows:

I. About 15,000 MW capacity consisting of 30, 60, 100, 110, 120, 140, 82.5, some of 200/210 MW units to be retired in a phased manner. These units are mainly non-reheat units (except 82.5, 110, 120, 140, 200/210 MW) with low efficiency and have already run for more than 25 years. The average efficiency of power generation would then appear to be better.
II. Renovate and modernise 200/210 and 500 MW units to upgrade their operating efficiency to near to design value.
III. Introduce supercritical/ultra-supercritical units of large size in future capacity additions, 13th plan and beyond.
IV. More penetration of renewable sources of energy (solar and wind).

All the above measures have been spelt out with a view to reducing carbon dioxide footprint from the power sector as a whole. All the above programmes are under way of implementation and are in different stages. Government of India has also taken a policy view point that in future all units in 13th plan and beyond, in the utility sector shall be with supercritical parameters. Supercritical units are about 2% better efficiency as compared to units with sub-critical parameters.

2 Efficiency Related Aspects

The average efficiency of operation of thermal power stations in the country is around 36%. The new units of supercritical designs are operating at around 40% efficiency whereas 500 and 600 MW subcritical units operate at around 38%

efficiency. The merit order dispatch in the grid is decided by the minimum variable price that is the cost of fuel. The system does not capture the efficiency of operation of the units meaning thereby the GHG emission aspects are not taken into account. The merit is decided based on the variable cost which has an element of cost of coal including transportation costs which can be more or less depending on the source and distance of transportation. To save fuel and consequently the carbon dioxide the merit order ought to be decided based on the operating heat rates of the machines.

The renovation and modernisation attempt was made by the government in the past and financial assistance was also provided to the states to affect the renovation and modernisation of various units with the help of CEA and Bureau of Energy Efficiency. Participation of the central public sector units such as National Thermal Power Corporation (NTPC), Power Grid Corporation of India Limited (PGCIL) were also sought.

Over the period of years of operation and the distribution business being a state subject, the tariffs of electricity not being commensurate with the cost, the distribution companies have accumulated huge losses. These losses had touched a figure of about 4 lac crores. A scheme called Ujjawal DISCOM Assurance Yojana (UDAY) has now been launched by the Govt of India for taking over existing debts of the state level power distribution companies with conditions of improving their efficiency, and reduction of T&D losses (both technical as well as commercial). There is a hope that the sector would generally improve and would become revenue surplus. After successful I supplementation of such a programme. The introduction of renewable sources of energy would drastically bring down the carbon dioxide emission since when these sources are contributing in the electricity generation; the coal consumption in the conventional thermal units is expected to come down.

3 Load Dispatch Philosophies

It may also be mentioned that distribution being a state subject, the dispatch from various generation units is controlled by the state load dispatch centres, and are thus susceptible to inefficient operation not really based on the best operation practices. Subcritical units are operated at a constant steam pressure and temperature down to a load called the control load, which is around 60%.

The effort was made to obtain the minimum heat rates on the turbine cycle side due to the maintenance of rated steam pressure and temperature even up to 60% loading on the unit. However, the turbine generally operated at lower efficiencies because of reduced steam flow rate at lower loads. This was not optimal to regain these lost efficiencies to the turbine, the sliding pressure mode of operation was evolved so that the steam turbines at lower pressure at reduced load increases the specific volume of steam enabling the turbine to operate at better efficiencies even at lower loads.

In case of machines operating at supercritical parameters, while operating on the sliding pressure mode, if the load comes down below 85% the unit comes down on subcritical parameters and the gain of efficiency for which the supercritical units were installed is completely lost. Therefore the large size supercritical units ought not to be operated on lower loads generally. The variations in the loads when required by load dispatch centres must be applied to the units other than supercritical ones. It is, however, observed that most of the state load dispatch centres are giving schedules of operation much lower than the 85%, to the supercritical units and these units thus operate at subcritical parameters. To avoid such erroneous operations, there is a need for training of manpower of the state generating and load dispatch centres and Independent Power Producers (IPPs) to operate the units in the correct operation mode. To improve upon the efficiencies, it may require modification in the legislations such as Electricity Act 2003 and subsequent regulations by the concerned regulators.

4 Grid Connectivity and Other Related Issues

The government has announced the target of solar installation of 100,000 MW and wind 60,000 MW by year 2022. To meet these optimistic targets, financing and technology issues are being addressed. The renewable purchase obligation (RPO) is now proposed to be made mandatory to be complied with by all the concerned entities including the distribution companies. The various thermal generators are also proposed to be mandated to install certain percentage of their installed capacity as solar power based through the amendments in the policy as well as Electricity Act 2003. This policy gives a good feeling that a large part of the energy should be drawn from the renewable sources of energy and minimum carbon dioxide emission will be let out as the coal quantity burned shall be reduced substantially due to increased generation by renewable sources.

The problem of introduction of greater proportion of renewable sources of generation however relates to the variable nature of solar and wind power. At a time when sun shines and the wind is blowing there is no necessity for the conventional generator to generate electricity and they will have to be backed down beyond the allowable limits. The conventional generators however are actually not designed for such variable generating mode and these machines are likely to be damaged during such operations. It has been the experience in the developed countries mainly in Europe that a large number of 800/900 MW conventional coal fired generators have suffered severe damages on generator insulations and the generator rotors have also suffered cracks. In India also some generating machines in some states have suffered such damages. Further at the time of peak load requirements generally the solar power is not available because typically the peak hours are morning and evening times when sun is not available in the right intensities. Supercritical units are therefore worst sufferers under such circumstances.

In view of the foregoing, following issues emerge:

1. To make the renewable power more acceptable from the grid operation point of view, some kind of storage system is necessary which will trigger in whenever the output of the machines comes down. The storage solutions however, are very expensive since it involves batteries of reliable nature and the cost of power generation increases three folds of the cost of generation without the storage. The question of affordability of renewable power will need to be addressed afresh. An alternative solution is that the renewable power developers have tie ups with hydro power plants which are on line and would trigger filling up the gaps. The availability of hydro power in the country is, however, becoming scarce. Since the exploitation of hydro potential itself is fraught with multiple difficulties involving difficult geological sites and, the approachability issues. In the past a few reservoir-based hydro stations have been converted to run-of-the-river projects by the states. This has resulted into a great loss to the development of appropriate type of hydro power in the country.
2. In accordance with the regulations in force, all generators including wind and solar plants are required to submit the schedule of generation for every 15 min time interval, i.e. 96 time intervals in a day in advance and also 24 h ahead, to the load dispatch centre to operate the grid efficiently. The wind generators, especially, so far have not come to terms with this requirement of the Central Electricity Regulatory Commission (CERC) regulations. CERC regulations had allowed plus minus 30% variations from the scheduled energy to be socialised and other violations beyond plus minus 30% will get penalised. Several institutions have come up in assisting the wind generators to predict every 15 min, the amount of generation. The generators should take advantage of such institutions.
3. There are other commercial issues to be settled relating to cross subsidies, regulatory assets and issues relating to separation of wire and content in the distribution sector.
4. It is seen that as the supercritical and subcritical units are being treated at par when it comes to merit order operation, and the supercritical units are required to be backed down also. The supercritical units are very delicate and sophisticated power generating units which are very sensitive to load fluctuations. These deteriorate very fast on efficiency and operate on subcritical parameters if asked to run at reduced loads. Accordingly, regulations must be in place to direct that the supercritical units will not normally be asked to back down and the backing down share shall be taken by inefficient and smaller units.
5. From considerations of efficiency, even the captive power plants also needs to be encouraged to build in larger unit sizes or else group captive plants to be encouraged to adopt larger and efficient units.
6. The merit order criterion should be based on efficiency not on the fuel price.

All the above factors will affect the efficiency of operation of the total system.

5 Conclusions

For the growth of power sector in India, installation of supercritical TPPs is recommended. The deployment of carbon capture and storage has not been encouraged in view of heavy cost and energy penalties. The following are the recommendations made for reductions of GHG emissions with adoption of supercritical technology.

a. In view of the fact that the demand of the power is fast growing, the installation of large size supercritical units is a must.
b. The captive generation needs to be encouraged only if they come in group captive with large size units in the range of 500–660 MW to maintain higher efficiency of power generation.
c. At the time of backing down of generation the supercritical units shall not be backed down below 80–85% generation to maintain high efficiencies.
d. Mass awareness programmes would need to be taken up and the components of the cost of generation need to be explained to the consumers.
e. Efforts shall be made to increase the temperature ratings of the supercritical units to around 700 °C from the present level of 600 °C. To attain still better efficiency.
f. The unit size also must be increased from 500/600 to 660/700/800 MW.

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Chapter 3
Low Carbon Technologies (LCT) and Carbon Capture & Sequestration (CCS)—Key to Green Power Mission for Energy Security and Environmental Sustainability

V.K. Sethi

Abstract Despite the fact that India has taken a giant leap forward in increasing the installed capacity from a mere 1367 MW in beginning of Independence era to over 303,100 MWe in June 2016, the renewable energy sources however contribute merely 14.1% with total capacity of over 42,800 MW. But this contribution has a major social and economic impact on rural and remote area population. The growth of clean energy technologies for mega Power generation, such as the Solar Mega Power under Jawaharlal Nehru Solar Mission, both Solar Thermal and PV, clean coal technologies, CCTs, i.e., supercritical power plants, integrated gasification combined cycle (IGCC), and fluidized bed combustion (FBC) are key to the success of Green Power Mission for India. Carbon capture and sequestration (CCS) is considered as the frontier Green Energy technology. CCS technology is still in the demonstration phase, and it is important that India is not left behind in this area. While there is a considerable amount of work already underway domestically, there may still be a need for research collaborations and knowledge sharing and transfer. Areas of research in CCS include development of new adsorbents, better process integration of capture equipment, and conversion of CO_2 to useful products, among others. The important challenge of energy penalty in CCS being faced worldwide can be met through the use of Concentrated Solar Power (CSP) for supplementing steam for regeneration in a solvent-based post-combustion CO_2 capture in thermal power plants. Low Carbon Technologies (LCT) and carbon capture and sequestration (CCS) are key factors for energy security and environmental sustainability, and the same are put forward in this chapter leading to an opportunity for course-correction in our thinking in Green Power.

Keywords Carbon capture · Sequestration · Amine solvent · Post combustion carbon capture · Concentrated solar plant · MEA solvent · Energy penalty

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Abbreviations

IGCC	Integrated gasification combined cycle
CCTs	Clean coal technologies
FBC	Fluidized bed combustion
CSP	Concentrated solar power
LCTs	Low carbon technologies
CERs	Certified emission reductions
HRSG	Heat recovery steam generator
STG	Steam turbine generator
TET	Turbine entry temperature
NTPC	National Thermal Power Corporation
APGENCO	Andhra Pradesh Generation Corporation
NAPCC	National Action Plan on Climate Change
DST	Department of Science and Technology
NPCS	National Program on Carbon Sequestration
RGPV	Rajiv Gandhi Prodyogiki Vishwavidyalaya
LCOE	Levelized cost of electricity
CEA	Central electricity authority
MEA	Mono ethanol amine
IS-STAC	Inter Sectoral Science & Technology Advisory Committee
UNFCCC	United Nations Framework Convention on Climate Change

1 Green Power Technologies—Clean Coal and Renewable Energy

We are aware that the global concern for reduction in emission of green house gases (GHG) especially CO_2 emissions are likely to put pressure on Indian Power System for adoption of improved generation technologies. Although India did not have GHG reduction targets under Kyoto Protocol, it has actively taken steps to address the climate change issues as per its Intended Nationaly Determined Contribution (INDC). It is estimated that the Green Energy projects undertaken by Indian Power Sector will generate over 600 million Certified Emission Reductions (CERs). Mitigation options for CO_2 reduction which have been planned to be taken up by Indian Power Sector include GHG emission reduction through adoption of cogeneration, combined cycle, clean coal technologies, and coal beneficiation. CO_2 emissions per unit of electricity generated are significantly high in India as large proportion of power generated comes from low sized, old, and relatively inefficient generating units which constitute over 50% of our total installed capacity. The technology upgradation through life extension of old polluting units is expected to increase the generating efficiency of these units thereby reducing CO_2 emissions.

A major thrust on CO_2 reduction on long term and sustainable basis would however come through adoption of advanced technologies of power generation like supercritical/ultra-supercritical power cycles, integrated gasification combined cycles (IGCC), fluidized bed combustion, and gasification technologies and so on (Reddy et al. 2003; Sharma and Sethi 2008). In addition to clean coal technologies, India is currently sitting on a gold mine of opportunities of energy farming for biodiesel production, biomass gasification for decentralized power generation and for alternative rural energy security to a large extent. The Planning Commission report on biodiesel (2003) advocates for a substitute of 20% of current diesel demand by biodiesel through energy farming on the available 11.2 million hectare land comprising of waste land, spare forest land and cultivation of Jatropha in rural areas and both sides of vast railway track. This would generate a vast sink for CO_2 while at the same time reduce exhaust emission through substitute of biofuels for transportation and other decentralized energy production needs.

1.1 Clean Coal Technologies

India is rich in coal and is the third largest coal producer in the world. Coal continues to be the dominating energy source and meets nearly 58% of total requirement of commercial energy. India has huge Gondwana (mainly Permian, 99.5%) and Tertiary (Eocene and Oligocene) coal deposits distributed in several basins located in peninsular and extra-peninsular regions of about 257 billion tons.

A beginning towards adoption of clean coal technologies in the form of supercritical units has already been made and it is foreseen that supercritical technology would almost universally be adopted for all large sized pithead units in the country. The attained efficiency gains of these technologies are likely to reduce the environmental emissions especially CO_2 significantly. Adoption of higher parameters for supercritical units after sufficient feedback and operational experience would further reduce these emissions to a great extent. A total additional efficiency of about 1.5–2% is normally achieved for adoption of supercritical parameters of 246 kg/cm^2 (g) and 537/565 °C, chosen for the supercritical power plant with unit size of the order of 660 MW. Adoption of still higher parameters would further enhance the efficiency. Attempts would also need to be made to further enhance the efficiency of conventional pulverized coal-fired plant by adoption of ultra-supercritical parameters. The main constraint being faced for adoption of these technologies is the availability of requisite material to withstand combination of high pressures and temperatures encountered. A consortium of several equipment manufacturers globally has pooled their resources to develop necessary materials to overcome the constraints for adoption of ultra-supercritical technology.

Another option for CO_2 reduction is the increased use of natural gas. This provides improvement in generation efficiency together with reduction in CO_2 emissions but would facilitate environmental pollution control only up to a certain extent. With addition of more and more generation capacity and also increasing CO_2 emissions from transport and other industrial sectors, progressive decarbonization of generation resources may have to be adopted in certain regions/areas. Already, natural gas is being used in a big way in the country for power generation and GT/CCGT stations accounted for about 9.4% of total generation today. The natural gas resource crunch being faced at present, even though there is quest for quick power generation restricts increased use of natural gas in Combined Cycle (CC) mode, limiting it to some specific priority areas only. Research work in this area to increase the generation efficiency of CC to an extent of 60% is already underway and this goal is likely to be realized in near future. These technologies can then be adopted as and when available. A much more efficient methodology of generating electricity from natural gas is on the anvil and this is fuel cell technology which looks more promising energy option in future.

Gasification of coal is the cleanest way of utilization of coal; while combined cycle power generation gives highest efficiency, the IGCC is thus categorized as an environmentally benign clean coal technology (Reddy et al. 2003). In an integrated combustion combined cycle power plant, the heating and partial oxidation of coal is done, such that synthesis gas or syngas (primarily hydrogen and carbon monoxide) is produced, which is subjected to the mechanisms of cooling and cleaning and then it is fired in a gas turbine generator. Whatever exhaust gases are produced, they are led through a heat recovery steam generator (HRSG), which forms steam that is sent to a steam turbine generator (STG) and from both the gas and steam turbines, while working in a combined cycle, power is produced. IGCC Technology is an option that provides high efficiency with hot gas cleanup. Low emission levels from IGCC plants have been demonstrated worldwide particularly with high turbine entry temperature (TET). IGCC is also regarded as a superior technology due to its capability to produce value added multipurpose fuels as well as the ease with which an IGCC plant could be retrofitted with a CCS plant.

A 6.2 MW domestic coal based IGCC pilot power plant has been set up in India by Bharat Heavy Electrical Limited (BHEL), which has contributed in technology assessment of gasification of high ash Indian coals. However commercialization of IGCC needs technology demonstration at an intermediate scale of about 100 MW to address the issues regarding hot gas cleanup, system optimization, etc., and to establish reliability and performance on continuous operation. This would also enable to get the performance of an optimum module for air blown gasification, which in multiples would constitute a commercial size plant in the range of 300–600 MW sizes. Three options are possible for the demonstration plant (CENPEEP 1997).

(a) Retrofit to an existing gas-based power plant with a coal gasifier system by utilizing the existing Power Island and operating the plant by replacing natural gas by coal gas.
(b) Converting an existing thermal power plant to IGCC mode by installing a Gasification Island and gas turbine.
(c) Setting up a green field IGCC plant.

Retrofit or conversion (options a, b) may be least cost options but will involve shut down of the existing power plant for carrying out modifications. In India due to acute power shortage, it is not desirable to shut down any of the existing power producing capability. If appropriate financing were available, it would be preferable to set up a green field IGCC plant. This could act as a demonstration plant for generating design data for upscaling and for testing various types of coals as well as processes of gas cleaning and establish the integration between Gas Island and Power Island. A green field plant would also be a good option for human resource development and training of manpower in this field. The National Thermal Power Corporation (NTPC), Bharat Heavy Electricals Ltd. (BHEL) and Andhra Pradesh Generation Corporation (APGENCO) have joined hands for execution of 100 MW IGCC plant. There is no doubt that IGCC can revolutionize the power generation scenario in India, once the commercial viability of technology with high ash coals is established for the proposed range of 100 MW plant. The success of the project will largely depend on maturity of fluidized bed gasification technology for high ash coals.

Integrated gasification combined cycle (IGCC) power plants can contribute to the mitigation of global energy issues. Though IGCC's present efficiency is up to 40%, still if further improvements in the process are made, then efficiency can reach up to and more than 50% in the near future through options like hot gas cleanup in excess of 560 °C, high turbine entry temperature, reduction in flame temperature and fuel dilution. Advanced technologies are being developed to improve the IGCC performance: new technologies for air separation and oxygen production, higher temperature gas cleaning methods, advanced gas turbines, and fuel cells. These technologies are being developed with the goal of raising thermal efficiency (higher heating value) to 50–60%.

Technological developments which are expected to be achieved by the next generation of IGCC projects and contribute to such cost reductions include:

- Utilization of dry coal feed system instead of slurry;
- "Warm" or hot gas cleanup systems; Warm gas cleaning processes are important to the overall IGCC system because at higher temperatures the gas maintains moisture content and some sensible heat.
- Improvement of gasifier refractory properties, resulting in longer life cycle;
- Ion transport membranes for air separation;
- Gas turbine inlet chilling where appropriate and effective;
- Advanced syngas turbines to increase efficiency and reduce NOx emissions;
- Improved reliability of key components and the overall system in general; and
- Reduced use of water.

1.2 Renewable Energy Technologies

Renewable Energy Technologies, particularly Solar PV are becoming increasingly important in our mix of power generation scenario. A target of 175 GW of Renewable Energy by 2022 is aimed at, which would make nonfossil fuel contribution to about 40% share in total installed generating capacity.

Among others wind power is the fastest growing electricity technology currently available. Wind-generated electricity is already competitive with fossil-fuel-based electricity in some locations, and installed wind power capacity in India is at a respectable level of 28,000 MW. Meanwhile, PV electricity, although currently at higher cost of delivered electricity, is seeing impressive growth worldwide. PV is particularly attractive for applications not served by the power grid. Advanced thin-film technology (a much less expensive option than crystalline silicon technology) is rapidly entering commercial-scale production, with 25 MW of manufacturing capacity already installed.

Renewable Energy Technology market in developing world is on the upward ramp. Many of these countries are attracted to the technologies that are having low gestation period and are cheaper in distributed generation mode. There is no doubt that R&D in the optimum mix of solar wind and biomass; having proven complementary nature in providing sustainable power, will have to be pursued more vigorously than today.

In the United States, national surveys show that over half of consumers in capital cities are willing to pay more for green power, and a number of power companies are now offering the same. We in India are also committed to achieve the target of 40% renewable by 2022, though coal is going to remain our main stay for next 2–3 decades. The issue before Indian energy sector today is use of high ash coal resource for optimum power generation with minimal environmental impact due to CO_2 emission.

The power sector already started witnessing a transition from conventional power generation technologies to the green power technologies. A major thrust on CO_2 reduction on long-term and sustainable basis would come through adoption of Renewable Energy Technologies and advanced cleaner technologies of power generation like supercritical/ultra-supercritical power cycles, integrated gasification combined cycles (IGCC), fluidized bed combustion (FBC)/gasification technologies, and other such green energy technologies. In the short-term, the focus is mainly on energy conservation measures and use of selected hybrid of renewable technologies like solar-wind-biomass.

2 Carbon Capture & Sequestration—A Frontline Technique for Combating Climate Change

2.1 Climate Change and Energy Generation

Climate change caused by the excessive industrial emissions of greenhouse gases (GHGs) is one of the gravest challenges facing our planet today. Studies have shown that there is no single option for combating this problem, but rather, a portfolio of measures, such as the increased use of renewable energy, improved energy efficiency, adoption of clean coal technologies which include carbon capture and sequestration will be needed.

CO_2 sequestration is a multifaceted approach involving capture of carbon from atmosphere followed by transportation, injection into favorable sites and post-injection monitoring. The favorable sites for storage of CO_2 must be reliable in the sense that CO_2 will be stored there permanently at least for 1000 years and no leakage is desirable. In this backdrop, we can say that coal bed and saline aquifer are the most suitable storage sites where CO_2 will be fixed permanently by chemisorptions and chemical reaction respectively.

Carbon capture and sequestration (CCS) is one among these measures, being a collection of technologies that may be able to reduce GHG concentrations beyond what would be possible from using other options alone. Carbon capture & sequestration would play an important role in reducing greenhouse gas emissions at the same time CCS would enable low carbon electricity generation from thermal power plants. As for example, CCS applied to a 500 MW unit, that emits 3 million tones of CO_2 per annum, would be equivalent to:

- Planting over 60 million trees and allow them to grow for 10 years
- Avoiding power related emissions of 0.3 million houses

However, several challenges must be overcome before large-scale CCS deployment becomes practical, including establishing the technical feasibility of long-term geological CO_2 storage, assessing the economics of capture, transport, and storage of CO_2 sensitizing the government, industry, and the common man to the potential of this technology, etc.

2.2 Current Climate Change Policies in India and Targets

In view of the fact that our energy generation in which coal-based power generation is our main stay, India takes the issue of global warming seriously. The government expenditure on climate change adaptation in India already exceeds 2.6% of GDP, knowing well that climate change is expected to have major impacts on water resources, agriculture, forests, etc., in India. To address the climate change issue, the Indian Prime Minister's Council on Climate Change released the National Action Plan on Climate Change (NAPCC) in 2008 according to which "India is determined that its per capita greenhouse gas emissions will at no point exceed that of developed countries even as we pursue our development objectives (Sethi et al. 2011)." Eight national missions for managing climate change have been set up:

1. National Solar Mission
2. National Mission for Enhanced Energy Efficiency
3. National Mission on Sustainable Habitat
4. National Water Mission
5. National Mission for Sustaining the Himalayan Ecosystem
6. National Mission for a "Green India"
7. National Mission for Sustainable Agriculture
8. National Mission on Strategic Knowledge for Climate Change

An important portion of the NAPCC deals with GHG mitigation in India's power sector. It points out that various measures for reducing GHG emissions from power plants, such as increasing the efficiency of existing power plants, using clean coal technologies, and switching to fuels other than coal where possible, must be viewed as being complementary and not mutually exclusive. CCS is however held in the NAPCC report as not being feasible at present, and concerns have been raised about the cost as well permanence of the CO_2 storage. While India is third largest emitter of carbon of the world after China and US but its per capita GHG emission is 1.7 Mt per annum which is well below the world average 4.5 Mt. To address the threat of climate change, India has declared in UNFC's Conference of Parties (COP-21) at Paris that:

- It will reduce its GHG intensity by 33–35% by 2030
- Power generation will be augmented through setting up of 175 GW of renewable energy, which will amount to 40% of the total energy mix.
- It will aim at carbon sequestration of the order of 2.5–3.0 billion tons of CO_2 through additional forest and tree cover. Focus on adaptation in agriculture, forest, water and livelihood will be accelerated
- India will not commit to any absolute cut in emissions as its economy is rather small, and no absolute cuts in greenhouse gases can be committed right now. Instead, it aims at cutting carbon intensity by 33–35% by 2030 from 2005 levels and grow to 40% the share of power generated from noncarbon fuels.

It has been recommended at several Forums of Ministry of Power that a better option could be carbon capture and sequestration (CCS) through the technologies of conversion of CO_2 into multipurpose fuels including biodiesel through Algae route.

2.3 R&D Efforts in CCS at RGPV, Bhopal

Most Indian Research and Development (R&D) activities related to CCS occur under the Department of Science and Technology (DST) of the Indian Ministry of Science and Technology. The DST set up the National Program on Carbon Sequestration (NPCS) Research in 2006, with a view to competing with other countries in this area with respect to both pure/applied research and industrial applications. Four thrust areas of research were identified under this programme, viz., CO_2 Sequestration through Micro algae Bio-fixation Techniques; Carbon Capture Process Development; Policy development Studies; and Network Terrestrial Agro-forestry Sequestration Modeling as detailed in DST reports on Projects under STAC/IS-STAC. The CO_2 capture, sequestration, and production of multipurpose fuels—hydrogen, methane, and biodiesel through algae route and through post-combustion CCS on a fossil fuel fired plant has been successfully demonstrated at the CO_2 sequestration pilot plant at the Madhya Pradesh State Technological University, the Rajiv Gandhi Prodyogiki Vishwavidyalya ('RGPV') installed under DST sponsorship (Savita et al. 2016a, b, c). This pilot project revalidated the possible use of the amine absorption system to strip the CO_2 from the flue gases but also validated the data on its efficiency for a power plant. A CO_2 Capture of over 93% has been achieved using MEA solvent of 20% concentration and the required heat for stripping captured CO_2 is 3.88 MJ per kg of recovered carbon dioxide, which is provided by the low pressure steam about 150 °C and 2 bar pressure from the associated boiler of 100 kg/h capacity. Although the stripper uses a low grade steam and some heat it contains was not used for generating power anyhow, it still causes 20% reduction of power output of boiler. Using the water gas shift reaction and a lignite/charcoal gasifier, about 18% (by volume) hydrogen is being produced in this pilot plant, paving the way to production of multipurpose fuels from captured CO_2.

Efforts are underway to produce methane from the stable CO and hydrogen so produced, in a catalytic converter. CO_2 from the stripper unit is also diverted to an open algae pond, where solar flux is concentrated using parabolic collectors and CO_2 is given in a regulated manner. Algal oil was extracted from algal biomass. R&D in the area of carbon sequestration need to be directed and country's policy needs to be dovetailed with the research. Emphasis needs to be given towards fixation and conversion of CO_2 into useful products, building materials, etc., rather than transportation and storage (Savita et al. 2016a, b, c). The simulation study has shown that if the technology of CO_2 Capture Recycling & Sequestration is applied on a 500 MW Coal-based Thermal Power Plant with 30% capture we will get benefits like (Sethi et al. 2010):

- Levelized cost of electricity or (LCOE) on a long-term basis calculated through simulation exercise for retrofitting would be Re. 1.05 per kWh. The energy penalty for 30% abatement would be 25%, if CO_2 is compressed and disposed. The total efficiency drop for 100% abatement is from 38.5 to 29.3%, i.e., 9.2%. The loss in generation due to use of steam in MEA process would be 15,000 kWh/h. The capital cost would be INR 15 million per MW. Simulations also showed the energy penalty for CO_2 capture from 500 MW flue gas from coal-fired power plants to be 0.01572 kWh/g mol CO_2.
- The simulation study further revealed that in a thermal power plant, if a slip stream of the flue gases is recycled then a 30% reduction of CO_2 would be achieved by direct abatement and recycle would result in a decline of fuel consumption by at least 7% and thereby reducing the CO_2 emissions by about 10% due to use of CO as fuel, thereby overall reduction of CO_2 by about 40% in the most cost effective manner. Thus the Net emission reduction when the recycled CO_2 is used in tandem with abatement would be 40% or down from 0.9 to 0.54 kg CO_2/kWh on a retrofitted Thermal Plant.

Efforts are underway to set up a CO_2 Capture & Sequestration plant on an actual coal thermal power plant through consortium approach. A scheme of retrofitting of existing 500 MW Unit with CO_2 Capture & Recycling of CO is being discussed with NTPC, TOSHIBA, and BHEL and the broad outline of the same would be as under (Fig. 1).

The pilot unit of this impact project is considered an important milestone in CO_2 Capture Technology for fossil-fired power plants. The size of the plant is selected well above lab scale unit so as to produce appreciable moles of CH_4 and H_2. This

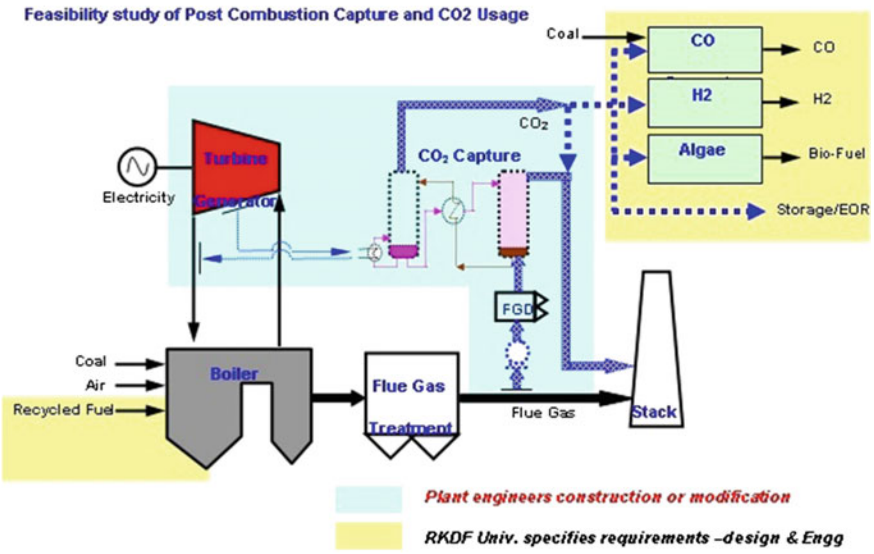

Fig. 1 Conceptual diagram of a power project with CCS

project is expected to resolve certain frontline issues in CO_2 sequestration such as energy intensive process optimization in terms of cost of generation and development of effective catalyst for methane, hydrogen, and biodiesel recovery through algae route. The scheme shows steam tap-off from turbine extractions which will cause energy penalty of the order of 15%. The same can be reduced to 4–5% level by combination of Solar Thermal generated Steam using a Concentrated Solar Plant (CSP) as shown in Fig. 2.

2.4 New Dimensions—Use of Solar for Reducing Energy Penalty

The proposed project discussed in previous paragraph will thus envision at establishment of the pilot plant of CO_2 capture and sequestration on for future development of technology so as to provide formidable support to the Govt. of India in the “Climate Change Mission.” This will also explore a new dimension of solar thermal energy input for steam generation for stripping of CO_2 and regeneration of CO_2 captured MEA to reduce energy penalty, a prime concern worldwide in CCS on actual thermal power plants with CCS. This will also pave way for development of a 500 MW Unit retrofitted with CCS with optimized configuration.

The thermal plants in India have a thermal efficiency of 35% and an emission ratio of 0.90 kg/kWh of CO_2 emissions as published by CEA. The reduction of 20% intensity would translate to a decrease by 0.20 kg/kWh of CO_2 emissions to

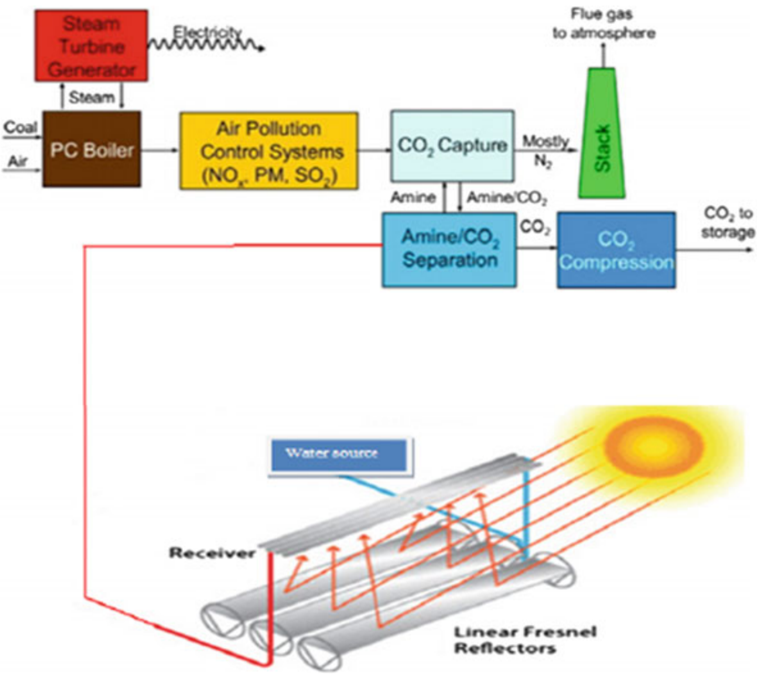

Fig. 2 Scheme of implementation of CO_2 Capture & Sequestration plant through integration with solar thermal

0.70 kg/kWh emissions by 2020. This decrease is possible by a combination of abatement and recycling measures.

However, the CO_2 reduction by an amine process of 30% CO_2 capture would mean an energy penalty of about 25% including about 15% for compression and pumping to deep reserves like mineral rocks, gas hydrates, and ocean. In any case the energy penalty in our case where CO_2 Sequestration is considered a far more appropriate option than CO_2 storage as the energy penalty still remains at level of 10–12%. The reduction of 4–5% can be demonstrated only after establishment of pilot scale CO_2 capture and sequestration plant integrated with concentrated solar power for carrying out system optimization studies (Fig. 2).

Expected and other physical outcomes of the project are:

- Establishment of the pilot plant of CO_2 capture and sequestration on an actual thermal power station for future development of technology so as to provide formidable support to the Govt. of India in the "Climate Change Mission."
- Erection, testing, commissioning of a coal-fired unit retrofitted with CCS and elaborate instrumentation and software for optimized configuration.
- The CO_2 so captured shall be sequestered to a depleted mine or conversion to hydrogen, methane, and biodiesel through algae route, as per location of power plant; case–to-case basis.

- The nonimaging concentrator technology based solar thermal plant will be used to produce steam for regeneration of MEA Solvent, so as to reduce energy penalty to about 5% from a level of 15%.

3 Conclusions

Low Carbon Technologies (LCTs) like renewable energy technologies will be increasingly important part of power generation mix over several decades though coal is going to remain our main stay.

Low Carbon Technology Vision for India together with strategies, challenges and opportunities in green power for energy security environmental sustainability are put forward in this chapter covering carbon capture and sequestration (CCS) as key factor.

Carbon capture and storage (CCS) will be a critical component in a portfolio of low-carbon energy technologies as we undertake ambitious measures to augment our power generation from fossil fuels and at the same time pursue our commitment towards combating climate change. At the current trends of increasing global carbon dioxide emissions by energy sector and the dominant role that coal continue to play in primary energy consumption, the urgency of CCS deployment is very important

The power sector already started witnessing a transition from conventional power generation technologies to the green power technologies. A major thrust on CO_2 reduction on long-term and sustainable basis would come through adoption of advanced technologies of power generation like supercritical/ultra-supercritical power cycles, integrated gasification combined cycles (IGCC), fluidized bed combustion/gasification Technologies, Renewable Energy Technologies, Biofuels, and other such green energy technologies. In the short-term, the focus is primarily on energy conservation measures and use of selected hybrid of “renewable” like solar-wind-biomass. The LCT plus CCS Technologies covered in this chapter may lead to an opportunity for course—correction in our line of thinking of our engineers and scientists in the arena of Green Power.

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Part II
Terrestrial Sequestration Options for CO_2

Chapter 4
Soil as Source and Sink for Atmospheric CO_2

Tapas Bhattacharyya, S.P. Wani, D.K. Pal and K.L. Sahrawat

Abstract Soils act as a major sink and source of atmospheric CO_2 and therefore have a huge role to play in the carbon capture and storage (CCS) activity. The soils capture and store both organic (through photosynthesis of plants and then top soils as decomposed plant materials and roots) and inorganic carbon (through the formation of pedogenic calcium carbonates). The sequestration of organic and inorganic carbon in soils and its follow-up require basic information of CCS in the soils and their appropriate management techniques. The most prudent approach to estimate the role of soils as source and sink for carbon should require information on the spatial distribution of soil type, soil carbon (soil organic carbon, SOC and soil inorganic carbon, SIC) and the bulk density (BD). To estimate the CCS of soils in spatial domains, we have used the agroclimatic zones (ACZs), bioclimatic systems (BCS) of India and the agro-ecosubregions (AESRs) maps as base maps. These three approaches of land area delineations have been used for various purposes at the national and regional-level planning. We have shown the utility of these maps for prioritizing areas for C sequestration in soils through a set of thematic maps on carbon stock. It will make a dataset for developmental programmes at regional as well as national levels, to address the role of soils in capturing and storing elevated atmospheric CO_2 due to global climate change.

Keywords CCS · Carbon sequestration · Soils · Thematic maps

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Abbreviations

SOC	Soil organic carbon
SIC	Soil inorganic carbon
BD	Bulk density
ACZs	Agro-climatic zones
BCS	Bioclimatic systems
AESRs	Agro-eco-sub-regions
SAT	Semi-arid tropical
Pg C	Peta gram carbon

1 Introduction

Soil carbon (both soil organic carbon, SOC and soil inorganic carbon, SIC) is important as it determines ecosystem and agroecosystem functions, influencing soil fertility, its water-holding capacity and other soil parameters. It is also of global importance because of its role in the global carbon cycle and the part it plays in the mitigation of atmospheric levels of greenhouse gases (GHGs), with special reference to CO_2.

The soil plays an important role for atmospheric CO_2 sequestration (Batjes 2011; Powlson et al. 2011; Banwart et al. 2013; Bhattacharyya et al. 2014; van Noordwijk et al. 2014). There has been a great deal of interest in mitigating the climate change due to global warming by sequestering and storing carbon in soil and its influence on soil quality and agricultural productivity (Powlson et al. 2011; Banwart et al. 2013; Bhattacharyya et al. 2014). Soils provide important ecosystem services at local as well as global levels and are the mainstay for crop production. Soils act both as sources and sinks for carbon (Bhattacharyya et al. 2008). With the challenge to feed a global population of 9 billion people by mid-century and beyond, it is essential to maintain the health and productivity of agricultural and rangeland soils (van Noordwijk et al. 2014). This can be done by maintaining, and wherever necessary, increasing the soil organic carbon, especially in tropical soils. The carbon sequestration in soil has been used to describe the process of increasing organic carbon stock with appropriate land management interventions. The process could be natural and/or human-induced to harness CO_2 from the atmosphere and to store it in ocean or terrestrial environments (i.e. in vegetation, soils and sediments) and in geologic formations (USGS 2008; Powlson et al. 2011). The reduction of atmospheric CO_2 by sequestration has been reported to have a great potential for shifting greenhouse gas (GHG) emissions to mitigate climate change, and soil is considered as an ideal reservoir, can store organic carbon to a great extent (Wang et al. 2010).

Interestingly, carbon sequestration has always been referred to in the literature with respect to its organic form, despite the fact that both organic and inorganic forms of carbon are involved in C sequestration. The aspects related to the formation of pedogenic $CaCO_3$ (PC), as an example of inorganic C sequestration, have a direct bearing to soil health (Bhattacharyya et al. 2004, 2008), especially in low quality, infertile soils in the semi-arid tropical (SAT) environments. Both vegetation and soils are the major sinks of atmospheric CO_2. Carbon stocks are not only critical for the soil to perform its productivity and environmental functions, but they also play an important role in the global C cycle. Soil C sequestration can improve soil quality and reduce the contribution of agriculture to CO_2 emissions.

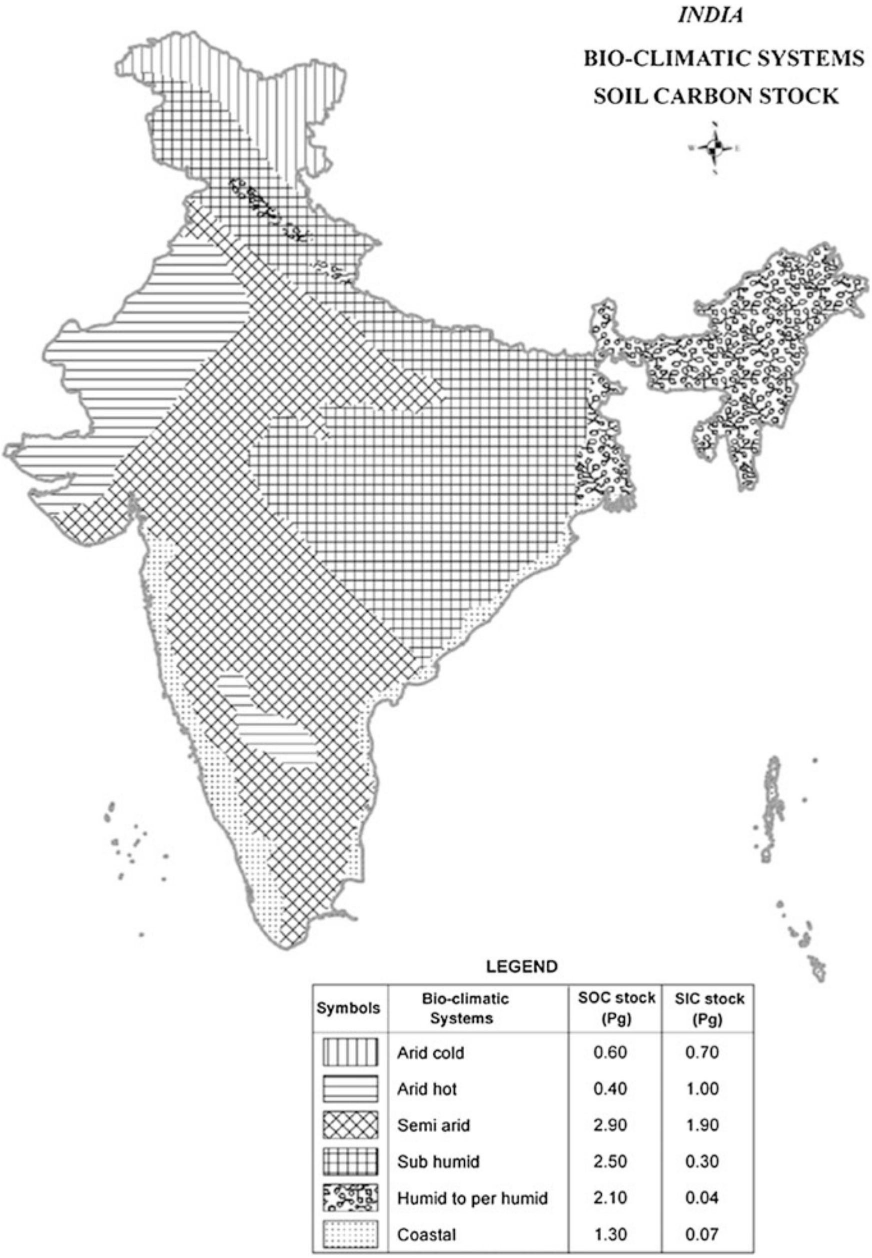
As the tropics comprise approximately 40% of the land surface of the earth, more than one-third of the soils of the world represent tropical areas (Eswaran et al. 1992). The global extent of such soils suggests that agricultural management practices can be developed in India for enhancing crop productivity and maintaining soil health through C sequestration. These may also have application in similar soils occurring elsewhere in the tropical and subtropical parts of the world. In this context, it was decided to prepare a synthesis on the potential of Indian soils to accumulate atmospheric CO_2 as evidenced by SOC and soil inorganic carbon (SIC) stocks. Moreover, the information on the factors and practices that favour C sequestration under diverse land use are put into context.

2 Soil: Source and Sink of Carbon

Soil carbon (SOC and SIC) is a major determinant of agroecosystem functions; it greatly influences soil fertility, water-holding capacity, and other soil quality parameters that influence overall productivity and sustainability. The main context for soil carbon management in tropical India is a relatively high amount of SOC (Jenny and Raychaudhuri 1960) (Table 1) and low amount of SIC, whereas soils in rest of the regions show a reverse trend (Bhattacharyya et al. 2000). The soils sequester both organic (through photosynthesis of plants and then to soils as decomposed plant materials and roots) and inorganic carbon (through the formation of pedogenic calcium carbonate) (Pal et al. 2000). The sequestration of organic and

Table 1 Soil carbon stocks in different bioclimatic systems of India (0–0.3 m soil depth)

Area million ha	SOC stock Pg	SIC stock Pg	Total C stock Pg	Carbon stock/million ha	
				SOC	SIC
Arid bioclimatic system					
52	1.0	1.7	2.7	0.019	0.033
Semi-arid bioclimatic system					
116.4	2.9	1.9	4.8	0.025	0.016
Sub-humid bioclimatic system					
105.0	2.5	0.3	2.8	0.024	0.003
Humid to per-humid bioclimatic system					
34.9	2.1	0.04	2.14	0.060	0.001
Coastal bioclimatic system					
20.4	1.3	0.07	1.37	0.064	0.003



Symbols	Bio-climatic Systems	SOC stock (Pg)	SIC stock (Pg)
▥	Arid cold	0.60	0.70
▤	Arid hot	0.40	1.00
▩	Semi arid	2.90	1.90
▦	Sub humid	2.50	0.30
▒	Humid to per humid	2.10	0.04
░	Coastal	1.30	0.07

Fig. 1 Carbon stocks in major bioclimatic systems in India (0–0.3 m soil depth). *SIC* soil inorganic carbon; *SOC* soil organic carbon (*source* Bhattacharyya et al. 2008)

inorganic carbon in soils and its estimation requires basic information on the processes that determine the C sequestration of soils (Batjes et al. 2007). The most prudent approach to estimate the role of soils as both C source and sink is to develop the spatial distribution of SOC and SIC in various agroclimatic zones, bioclimatic systems and agroecosystem sub-regions (Victoria et al. 2012; Batjes 2011; Bhattacharyya et al. 2008). Carbon as SOC and SIC storage has been reported to be related to climate (temperature and rainfall). The carbon storage values for different bioclimatic systems have been collated and are shown in Fig. 1.

The arid bioclimatic system is characterized by low annual rainfall (<500 mm) (Bhattacharjee et al. 1982) and does not support dense vegetation, resulting in low organic C status of the soils. This bioclimate is divided into cold and hot arid depending on atmospheric temperature (Bhattacharyya et al. 2000) and within the cold arid bio climate, the Ladakh plateau is colder than the northern Himalayas. Lower atmospheric temperature at the subzero levels that cause hyper-aridity does not support vegetation, which is in contrast to that found in the western region of the northern Himalayas. This is the reason for more SOC stock in the cold arid bioclimate (Table 1). Following U.S. soil taxonomy (Soil Survey Staff 2006), total SOC stock of Indian soils in the first 1.5 m depth is estimated at nearly 30 Pg, whereas that of SIC as nearly 34 Pg. The SOC and SIC stocks in five bioclimatic zones (Bhattacharyya et al. 2008) show that SOC stock is two and one-half times greater than the SIC stock in first 0–0.3 m soil depth. Although the presence of $CaCO_3$ in the humid and per-humid region is due to inheritance from strongly calcareous parent material, usually on young geomorphic surfaces (Velayutham et al. 2000), the SIC stock in dry bioclimates is relatively large (Bhattacharyya et al. 2008). The SIC stock increases with depth in all soil orders (except for the Ultisols) of dry climates, which cause more calcareousness in the subsoil (Pal et al. 2000).

3 Prioritizing Areas for Carbon Sequestration in Soils

Carbon stock in soil depends largely on the aerial extent of the soils besides other factors such as carbon content, depth and bulk density (BD). Even with a relatively small carbon content (0.2–0.3%), the SOC stock of arid and semi-arid systems indicates a high value. This is due to a large area of the dry tracts. Therefore, the carbon stock per unit area (Pg/mha) should ideally be considered to identify the influence of soil and/or management parameters for carbon sequestration in the soils. A threshold value of 0.03 Pg SOC/mha has been found to be effective in finding out a system (agriculture, horticulture, forestry) which sequesters sizeable quantity of organic carbon in the soils (Bhattacharyya et al. 2008).

Criteria such as SOC stock per unit area as well as point data for individual soils indicate that vast areas in the arid (AESR 3, part of ACZ 10), semi-arid and drier parts of the sub-humid bioclimatic systems (BCS) of the Indian subcontinent are low in SOC and high in SIC stock and thus should get priority for organic carbon management. The total prioritized area has been worked out as 155.8 m ha.

It has been reported that increase of OC enhances the substrate quality of soils. The dominant black soils (Vertisols and their associated red soils) in the semi-arid tropics (SAT) are rich in smectites (Pal et al. 2000) which results in improving substrate quality of soils resulting in 2–3% carbon sequestration (Bhattacharyya et al. 2006). In view of better substrate quality of these dominant soils in the arid (southern India, AESR 3), semi-arid and dry sub-humid tracts of the country, a modest SOC content of 2% gives an estimate of SOC stock as 14.02 Pg. This value is 3.7 times more than the existing SOC stock of the prioritized area (Bhattacharyya et al. 2008). The SOC stock has increased from 34 to 118% over a period of nearly 25 years in SAT due to adoption of the management intervention and the substrate quality (Bhattacharyya et al. 2007). Thus with appropriate management interventions in maintaining the capability of productive soils and also in improving the less productive soils, organic carbon storage capacity of Indian soils can be enhanced. Such management interventions have helped in the dissolution of native SIC ($CaCO_3$) due to increase in pCO_2 in the soil and contribute partly to the overall pool of SOC (Bhattacharyya et al. 2004).

4 Concluding Remarks

Although the unique role of soils as a potential sink in mitigating the effects of atmospheric CO_2 has been conceived, the present study indicates the sequestration of atmospheric CO_2 in the form of SIC (pedogenic carbonate) and its subsequent important role in enhancing SOC in the drier parts of the country through management interventions. The study also points out that the soil can act as a potential medium for CCS. This tool (thematic maps on soil C stock) may help planners in prioritizing C sequestration programmes in different dry BCS representing various ACZs and AESRs of the country.

Soils of the tropical Indian environments are endowed with diverse, generally good substrate quality, and they are under favourable environmental conditions, as is evident from their considerable potential to absorb atmospheric CO_2 as SOC. The formation of pedogenic $CaCO_3$ (as SIC) and its subsequent role in enhancing the potential of soils to sequester SOC in the drier regions of the country illustrates a unique process involved in sequestering atmospheric CO_2. Major soil types generally show resilience to spring back to normal productive state with appropriate management interventions by farming communities with the support from national and international institutions (Bhattacharyya et al. 2007; Bhattacharyya 2015). These soils have provided a sustainable foundation for India's growing self-sufficiency in food production, and they generally maintain a positive organic C balance in the longer term. In view of a good potential for C sequestration by major zeolitic and nonzeolitic soils, the present SOC stock of about 30 Pg can be further increased under improved management of soil, water, crop and nutrients in various diverse production systems. These case studies indeed may serve as a model elsewhere under similar soil and climatic conditions in the tropical world to maintaining soil heath and productivity under climate change through C sequestration.

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Chapter 5
Soil Carbon Stock and CO_2 Flux in Different Ecosystems of North-East India

P.S. Yadava and Amrabati Thokchom

Abstract Soil carbon stock and soil CO_2 flux are the major components of carbon budget and carbon cycle in the different terrestrial ecosystems of the world. Soils are the largest carbon reservoirs of the terrestrial carbon cycle. About three times more carbon is contained in soils than in the world's vegetation and soils hold double the amount of carbon that is present in the atmosphere. Soil can be source or sink of greenhouse gases depending on land use and management. The detailed information on soil carbon stock and soil CO_2 flux and its controlling factors is critical for constraining the ecosystem C-budget and for understanding the response of soils to changing land use and global climate change. Therefore, we examined the soil carbon stock and CO_2 flux in the different terrestrial ecosystems, i.e. forest, bamboo and grasslands of north-east India and its controlling of biotic and abiotic factors. Soil organic carbon was found to be highest in bamboo and followed by grassland and forests whereas reverse trend was observed in rate of soil CO_2 flux which was in the order of forest > grassland > bamboo forest and were influenced by biotic and abiotic factors.

Keywords Abiotic factor · Biotic factor · North-east India · Soil carbon stock · Soil CO_2 flux

Abbreviations

SOC	Soil organic carbon
LULUC	Land use, land use changes in forestry
Mg C ha^{-1}	Mega grams carbon per hectare

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1 Introduction

Soil is a major source for atmospheric carbon dioxide (CO_2). It represents the largest terrestrial stock of C, holding between 1400×10^{15} g (Post et al. 1982) and 1500×10^{15} g C (Batjes 1996). This is approximately twice the amount held in the atmosphere and three times the amount held in terrestrial vegetation. In most soils (with the exception of calcareous soils) the majority of this carbon is held in the form of soil organic carbon (SOC) (Batjes and Sombroek 1997). Thus changes in terrestrial SOC stocks (both increases and decreases) can be of global significance and may either mitigate or worsen climate change. SOC is vital for ecosystem function, having a major influence on soil structure, water-holding capacity, cation exchange capacity and the soils ability to form complexes with metal ions and to store nutrients (van Keulen 2001). Appropriate management of soils to increase SOC levels can, therefore, increase the productivity and sustainability of agricultural systems (Cole et al. 1997). Management of soil, therefore, plays important role in the mitigation of greenhouse gases (GHGs). United Nations Framework Convention on Climate Change and the Kyoto Protocol, which refer to the removal of C from the atmosphere by the improved management of agricultural soils (Article 3.4.) and by forestry activities, including C storage in forest soils (Article 3.3.) recognizes this.

The amount of soil C is determined by balance between the rate of soil organic C input in leaf and root biomass and its mineralization (Gregorich and Janzen 1996). Variations in soil C stocks are related to a number of environmental factors as well as human-induced factors. SOC holds a very important role in global C-cycle, as it is the largest terrestrial C pool. SOC is one of the most important indicators of soil fertility, productivity and quality. Decline in SOC creates an array of negative effects on land productivity. Since soil contains a significant part of the global carbon stock, the role of soil as a sink for carbon under different land use management practices in terrestrial ecosystems is necessary in understanding the global C-cycle. According to the IPCC, among the different carbon sinks, soil acts as one of the best option for reducing the atmospheric CO_2 and has recognized SOC pool as one of the five major carbon pools for the Land Use, Land Use Change in Forestry (LULUCF) (paragraph 21, the annex to draft decision 16/CMP.1). Soil plays a major role in global carbon cycle as it is an important pool of active carbon (Meliloet al. 1995; Prentice et al. 2001). Each ton of soil organic matter build removes about 3.667 tons of CO_2 from the atmosphere (Bowen and Rovira 1999). Maximum SOC sequestration in soils of different land use systems is an effective strategy for reducing and removal of atmospheric CO_2 and improving the quality of soil (Lalet al. 1999).

Soil CO_2 flux is the production of CO_2 by an organism and the plant parts in the soil. Soil CO_2 efflux differs among ecosystems and also varies with environmental conditions. Soil CO_2 flux has large variations because of the influences of individual biotic and abiotic factors in the different ecosystems. It is a composite process integrating two major carbon fluxes, i.e. autotrophic respiration of plants root and heterotrophic respiration through the soil microbial activities and is influenced by multitudes of environmental factors (Zhao et al. 2013). It provides the main carbon efflux from terrestrial ecosystems to the atmosphere and is therefore an important component of the global carbon cycle balance (Buchman 2000; Schlesinger and Andrews 2000).

Small changes in soil CO_2 flux across large areas can produce a great effect on CO_2 atmospheric concentration and provide a potential positive feedback between increasing temperature and enhanced soil respiration that may ultimately accelerate global warming (Schlesinger and Andrews 2000). Therefore, detailed information on soil CO_2 flux and its controlling factors is critical for constraining the ecosystem C-budget and for understanding the response of soils to changing land use and global climate change (Han et al. 2007). In this paper soil carbon stock and CO_2 flux in the different terrestrial ecosystems of north-east India have been discussed and its interrelationship with biotic and abiotic factors.

2 Soil Organic Carbon Concentration (%) Under Different Land Use Change in North-East Region

North-eastern region of India has wide range of ecological habitats varying from grassland to dense forests, disturbed secondary *Jhum* fallows to almost virgin natural forests (Rao 1994). The SOC content is expected to be highly variable across the region depending on the different climatic conditions, topography, rainfall pattern, vegetation, land use pattern and high diversity. Among the components of global change, land use change has the greatest impact on terrestrial ecosystems and in north-east India the most important land use change resulted from the shifting cultivation practices. On an average 36.64% of the total geographical area is degraded as a result of shifting cultivation in north-eastern India, which is almost twofold more than the national average of 20.17% (Bhatt et al. 2006). The average loss of SOC is reported to be 703 kg ha^{-1} due to soil erosion in north-east India (Ramesh et al. 2015). SOC concentration under different land use changes in the north-east India is set in Table 1.

SOC concentration varied from 0.34 to 4.30% in different land uses in north-east India. Highest concentration of SOC was recorded for broad-leaved forest of Meghalaya (4.30%) followed by subtropical forest of Manipur (3.50%) and recent slash and burn forest sites (2.37%). Slash and burn site has higher concentration of carbon in soil because of addition of burnt or partially burnt organic matter added to the soil during slash and burnt treatment. Low concentration of soil carbon in the disturbed forests may be attributed to low litter production as well as slow rate of litter decomposition.

Thus it shows that the concentrations of carbon in the soil are highly linked with microenvironment, litter dynamics, altitude and type of vegetation. Release of nutrient from litter through decomposition process is recognized as an important part of carbon released in the soil. Therefore, an ecosystem that can restore the soil quality and maintain the long-term sustainability needs to be identified in the highly degraded hilly region of north-east India.

Table 1 Soil organic carbon concentration (%) under different land use change in north-east India

S. no.	Land use type	Soil organic carbon concentration (%)	Soil depth (cm)	Location	References
1.	Wet and temperate forest	0.97	0–30	Manipur	Singh and Yadava (1991)
2.	Tropical wet every forest, undisturbed	2.23	0–30	Arunachal Pradesh	Barbhuiya et al. (2004)
3.	Disturbed forest	1.23	0–30	Arunachal Pradesh	Barbhuiya et al. (2004)
4.	Highly disturbed forest	0.89	0–30	Arunachal Pradesh	Barbhuiya et al. (2004)
5.	Protected *Dipterocarpus* forest	0.69	0–30	Manipur	Devi et al. (2006)
6.	Slash and burn *Dipterocarpus* forest	2.37	0–30	Manipur	Devi et al. (2006)
7.	Pine forest	0.34	0–30	Manipur	Devi et al. (2006)
8.	Mixed forest	0.35	0–30	Manipur	Devi et al. (2006)
9.	Grassland	1.14	0–30	Manipur	Singh and Yadava (2006)
10.	Agro ecosystem	1.07	0–30	Manipur	Singh and Yadava (2006)
11.	Subtropical mixed oak forest	3.50	0–30	Manipur	Devi and Yadava (2009)
12.	Slash and burnt tropical forest	2.38	0–30	Manipur	Binarani and Yadava (2010)
13.	Protected tropical forest	1.20	0–30	Manipur	Binarani and Yadava (2010)
14.	Pine forest	2.10	0–30	Meghalaya	Mishra (2011)
15.	Broad-leaved forest	4.30	0–30	Meghalaya	Mishra (2011)
16.	Plantation forests	1.00	0–20	Meghalaya	Thapa et al. (2011)
17.	Mixed bamboo forest	1.21	0–20	Meghalaya	Thapa et al. (2011)
18.	Semi-evergreen forest	1.29	0–20	Meghalaya	Thapa et al. (2011)
19.	Agricultural landscape	1.69	0–30	Arunachal Pradesh	Yumanm et al. (2013)
20.	Dipterocarp forest	1.15	0–30	Assam	Rabha et al. (2014)

3 Soil Organic Carbon Storage in Different Ecosystems of North-East Region

The forest ecosystems store more than 70% of the global SOC and the forest SOC pool is determined by balance between C inputs from animals, plants and microorganisms and the carbon released during decomposition. SOC storage varied from 14.77 to 18.75 Mg ha^{-1} in tropical forests; 21.36 to 22.56 Mg ha^{-1} in sub-tropical forests and 33.87 Mg ha^{-1} in temperate forest at a depth of 0–30 cm. (Table 2). The higher proportion of SOC in the temperate forest soils is because of slower decomposition rate of plant litter being low temperature while in tropical forest the dead biomass rapidly decomposes in the warm, humid conditions.

In bamboo forest, the SOC stock (0–30 cm) was reported to be 51.91–84.23 Mg ha^{-1} in bamboo forest of Mizoram, 55.95 Mg ha^{-1} in Barak Valley of Assam, 57.30 Mg ha^{-1} in Manipur and 51.20–56.87 Mg ha^{-1} in Arunachal Pradesh. The SOC was reported to be 57.28 Mg ha^{-1} in protected and

Table 2 Mean organic carbon content in the soils of different forests of north-eastern India

S. no.	Forest type	C-stock (Mg C ha^{-1})	Location	References
1.	Tropical wet evergreen forest	18.75	Arunachal Pradesh	Barbhuiya et al. (2004)
2.	Tropical forest	14.77	Moreh, Manipur	Yadava (2015)
3.	Subtropical oak forest	21.36	Imphal, Manipur	Yadava (2015)
4.	Subtropical pine plantation	22.56	Imphal, Valley, Manipur	Yadava (2015)
5.	Temperate forest	33.87	Senapati, Manipur	Yadava (2015)

Table 3 Mean organic carbon content in the soils of different bamboo and grassland ecosystems of north-eastern India

S. no.	Ecosystem type	C-stock (Mg C ha^{-1})	Location	References
1.	*Shizoastachyum pergracile* bamboo forest	57.30	Moreh, Manipur	Thokchom and Yadava (2016a)
2.	Village bamboo groove	55.95	Barak valley, Assam	Nath et al. (2009)
3.	Bamboo forest	51.20–56.87	Arunachal Pradesh	Arunachalam and Arunachalam (2002)
4.	Bamboo forest	51.91–84.23	Mizoram	Vanlalfakawma et al. (2014)
5.	*Imperata* grassland	69.75	Arunachal Pradesh	Arunachalam and Arunachalam (2002)
6.	Unburnt grassland Burnt grassland	57.28 44.74	Imphal valley, Manipur	Thokchom and Yadava (2016b)

Table 4 Profile soil organic carbon stock in forest ecosystems of Manipur, N.E. India (Mg C ha^{-1})

Soil depth (cm)	Tropical forest	Subtropical forest	Temperate forest
0–30	11.90 ± 2.31	24.00 ± 1.63	30.8 ± 1.82
30–50	4.14 ± 2.03	16.80 ± 2.54	12.4 ± 1.68
50–70	3.90 ± 1.32	8.81 ± 2.14	7.20 ± 1.43
70–100	1.70 ± 1.16	8.30 ± 1.32	4.73 ± 1.37
Total	21.64 ± 4.46	57.91 ± 7.44	65.13 ± 11.78

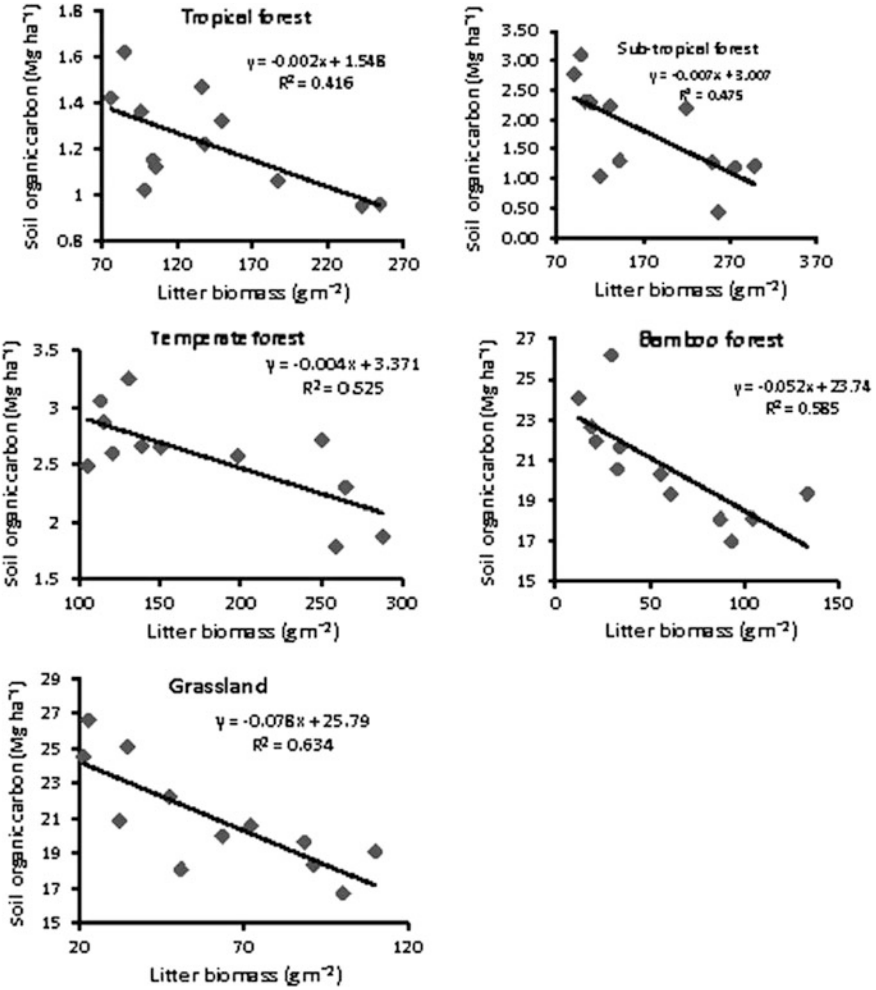

Fig. 1 Relationship of soil organic carbon (Mg ha^{-1}) stock with litter biomass (gm^{-2}) in tropical forest, subtropical forest, temperate forest, bamboo forest and grassland ecosystem at $P < 0.001$

44.74 Mg ha^{-1} in burnt grassland of Manipur and 69.75 Mg ha^{-1} in Arunachal Pradesh (Table 3).

It seems soils of grassland and bamboo store more carbon than that of tropical and subtropical forest which may be due to leaching out of minerals rapidly in the tree forests. The soil carbon stock declines on burning because of combustion of surface litter inputs and the decrease in the root activity.

SOC stock has been estimated up to 1 m soil depth, i.e. 0–30, 30–50, 50–70 and 0–100 cm in a year in tropical, subtropical and temperate forest types. SOC were recorded highest in upper soil depth 0–30 cm soil depth and decreased with increase in soil depth in all the sites because of high rate of litter accumulation and faster decomposition of litter in the upper surface (Table 4).

The SOC stock in the soil was related with the litter biomass in all the ecosystems as given by the linear regression equation as given in Fig. 1. The relation shows a significant negative correlation in all the ecosystems. It explains 64–80% variability in the SOC stock in all the ecosystems due to variability in the carbon stock of litter biomass. Thus it shows that litter production has been the controlling factors in the storage of carbon in the soil. Beside this SOC is also influenced by the rate of litter decomposition.

4 Soil CO_2 Flux in Different Ecosystems of North-East India

Annual soil CO_2 flux varied from 8.07 to 10.29 Mg C ha^{-1} year^{-1} in the different forest ecosystems of Manipur and was in the order of tropical > subtropical > temperate forest (Table 5). Annual soil CO_2 was recorded to be 6.81 Mg C ha^{-1} year^{-1} and 6.99 Mg C ha^{-1} year^{-1} in bamboo and grassland respectively. The amount of CO_2 released from soil into the atmosphere was higher for forest ecosystems than that of grassland and bamboo forest. This may be attributed to the high microbial activities and soil organic matter which was highest in forests

Table 5 Annual CO_2 emissions from the soils in different forest ecosystems in north-eastern India

S. no.	Ecosystem type	Mg C ha^{-1} year^{-1}	Location	References
1.	Tropical moist deciduous forest	10.29	Moreh, Manipur	Thokchom and Yadava (2014)
2.	Subtropical forest	9.37	Imphal, Manipur	Yadava (2015)
3.	Temperate forest	8.07	Senapati, Manipur	Yadava (2015)
4.	Bamboo forest	6.81	Moreh, Manipur	Thokchom and Yadava (2014)
5.	Grassland	6.99	Imphal, Manipur	Thokchom and Yadava (2014)

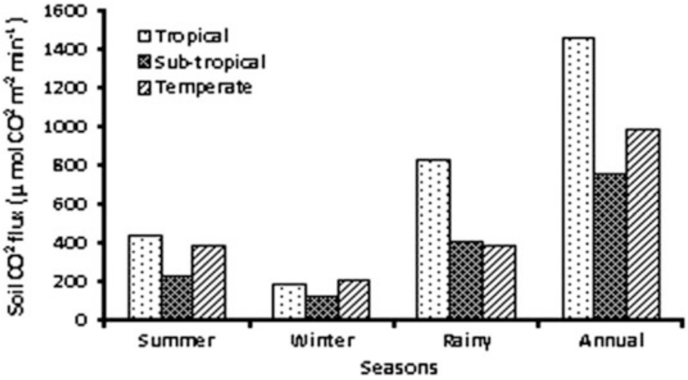

Fig. 2 Rate of soil CO_2 flux in different seasons in all the forests ecosystems

followed by grassland and bamboo ecosystem. Thus the forest soil contributes more CO_2 emission to the atmosphere than those of grassland and bamboo soils in spite of high SOC in latter vegetation.

Soil CO_2 flux showed remarkable seasonal variation in all the forest ecosystems. It was highest during rainy season followed by summer and minimum in winter in the three different ecosystems, which may be due to similar climatic conditions prevailing in the region in all the forest ecosystems (Fig. 2). Maximum soil CO_2 flux during rainy season results from spurt mineralization of the labile soil organic matter that has accumulated during the dry period and which is available to microorganisms after rewetting of the soil. The moist soil condition promoted the physiological activities of soil microbes and root respiration resulted in the increase of soil CO_2 flux.

The relationship between rate of soil CO_2 flux (Mg C ha^{-1} $year^{-1}$) and soil properties, i.e. soil temperature ($X1$), soil moisture ($X2$) and SOC ($X3$) has been analysed by multiple regression in all the study sites and is summarized as follows:

***Dipterocarpus (Tropical)* forest site**

$Y = -20.479 + 52.440X1 + 24.329X2 - 5.629X3$,

($r1 = 0.57$; $r2 = 0.97$; $r3 = 0.84$) at $P < 0.01$.

Temperate forest

$Y = -47.925 + 0.425X1 + 0.465X2 + 0.032X3$

($r1 = 0.72$; $r2 = 0.61$; $r3 = 0.85$) at $P < 0.01$.

Grassland site

$Y = -683.446 + 1.229X1 + 3.557X2 + 498.496X3$,

($r1 = 0.81$; $r2 = 0.68$; $r3 = 0.97$) at $P < 0.01$.

Bamboo forest site

$Y = -104.406 + 4.301X1 + 0.393X2 + 163.729X3$,

($r1 = 0.93$; $r2 = 0.95$; $r3 = 0.90$) at $P < 0.01$.

The study shows that significant positive relationship between soil CO_2 flux rates and variables: soil moisture, soil temperature and SOC have strong influence on the release of CO_2 into the atmosphere from the soil in the three ecosystems. The 68–92% variation in soil CO_2 flux rate is explained by these three variables.

Thus it shows that soil temperature, soil moisture and SOC are the controlling factors on the emission of CO_2 from the soil in all the three terrestrial ecosystems.

5 Conclusions

North-eastern part of India has a widely different vegetation types ranging from grassland to dense forests, abandoned secondary *jhumlands* (Shifting Cultivation) to virgin forests. Thus change in land use pattern will have long-term implication on the carbon management strategies in the north-east India. Control burning and deforestation of forests is advocated to minimize CO_2 release from the soil.

SOC stock was recorded to be in the order of temperate > subtropical and tropical forests. However, grassland and bamboo forest soils store more C than that of forest soils. In case of soil CO_2 flux rate it shows a reverse trend, i.e. higher in forest soils than that of grassland and bamboo soils. SOC stock and soil CO_2 flux rate are highly variable and influenced by vegetation type, rainfall and other climatic factors in the north-east region.

The study indicates that plantation of bamboo and implementing efficient CO_2 sequester tree species in the degraded ecosystem would result in enhancement of carbon storage in the soil and reduction of CO_2 emission from the soil. Thus change in land use pattern will have long-term implication on the carbon management strategies in the north-east India.

These findings will enable us to accurately estimate regional carbon fluxes and carbon budget by taking into the consideration the biotic and abiotic variables in different ecosystems of north-east India. In the event of growing threats of global warming due to GHGs emission, reducing CO_2 emission by soil and increasing soil carbon stock is of prime importance. Therefore, carbon sequestration in the soil components can be one of the attractive strategies for terrestrial ecosystems in north-east India to mitigate the climate change at regional and national levels.

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Chapter 6
Baseline Data of Stored Carbon in *Spinifex littoreus* from Kadmath Island, Lakshadweep

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Abstract Sand dune vegetations have several ecosystem services of which carbon storage and sequestration play a major role in the domain of climate change. Stored Carbon in the Above Ground Biomass and Below Ground Biomass of *Spinifex littoreus* collected from Kadmath Island (U.T. of Lakshadweep) were estimated during March 2016. Soil Organic Carbon was also monitored simultaneously to evaluate the stored organic carbon in the underlying soil. The observed data shows that density or biomass per unit area of the species plays a crucial role in regulating the carbon pool in the coastal zone.

Keywords Stored carbon · AGB · BGB · *Spinifex littoreus* · Kadmath Island

Abbreviations

AGB	Above ground biomass
BGB	Below grown biomass
SOC	Soil organic carbon
TCD	Thermal conductivity detector

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BA	Basal area
AGC	Above ground carbon
BGC	Below ground carbon
PgC	Peta grams of carbon
ANOVA	Analysis of variance

1 Introduction

Carbon dioxide (CO_2) once emitted to the atmosphere, takes centuries for natural removal. Every 4 giga tonnes of carbon (GtC) emitted to the atmosphere results in a rise of one ppm of CO_2 in the atmosphere (Moriarty and Honnery 2010). Although most of the carbon dioxide is absorbed by the oceans, some 20–40% will remain in the atmosphere for even longer periods (Archer et al. 2009). Researchers conclude that climate effects of CO_2 released to the atmosphere will persist for a long time into the future. Terrestrial ecosystems hold a lot of carbon, approximately 500 Peta grams of carbon (Pg C) in plant biomass, and 2000 Pg C in SOC. Oceans contain even more and the atmosphere, now with about 785 Pg C, connects all of these pools (Janzen 2004). Due to high primary productivity rates, relatively high nutrient concentrations and coverage of the earth surface, coastal margins are important components of the oceanic carbon cycle (Ronald et al. 2001; Sathyanathan et al. 2009; Sunkur and Appadoo 2011). Most of coastal zone surrounding the Arabian Sea has sandy substratum. The environmental condition is extremely harsh due to high temperature and salinity. The Kadmath Island in Lakshadweep support few sand dune vegetations, which include specialized plant community that grows on the sandy shore beyond high tide level. *Spinifex littoreus* is one such common plant growing in this region. The plant is commonly found growing on the fore and mid-shore dune region of the sandy shore.

The species grows extensively on sandy shore where the sand is medium to fine between the range of 1.8–2.51. The water holding capacity of the fine sand is more and this is made available to the plant by deep rooting system. It can absorb water from a depth of 60–70 cm below the surface. The pH necessary for the growth of the plant varies from 4 to 5. The plant can also grow under low nutritional conditions. As such sand dune soils are generally low in the macronutrients but they appear to have adequate quantities of the micronutrients, (Chapman 1976). The organic requirements of the plant are also very low, as the plant naturally grows on a low nutrition of 4.76–5.47% of organic matter. Kadmath island, situated in U.T. of Lakshadweep sustains a large biomass of *S. littoreus* in the supra littoral zone. The present paper aims to study the stored carbon in the Above Ground Biomass (AGB) and Below Grown Biomass (BGB) of the species and understand the effect of variation of biomass on the Soil Organic Carbon (SOC).

2 Materials and Methods

The entire network of the present study consists of few important steps namely, selection of station, collection of species, biomass and stored carbon estimation in the AGB and BGB portions of the plant material separately, SOC estimation in substratum with variable biomass and finally statistical analysis to reach a conclusion.

(a) Selection of stations

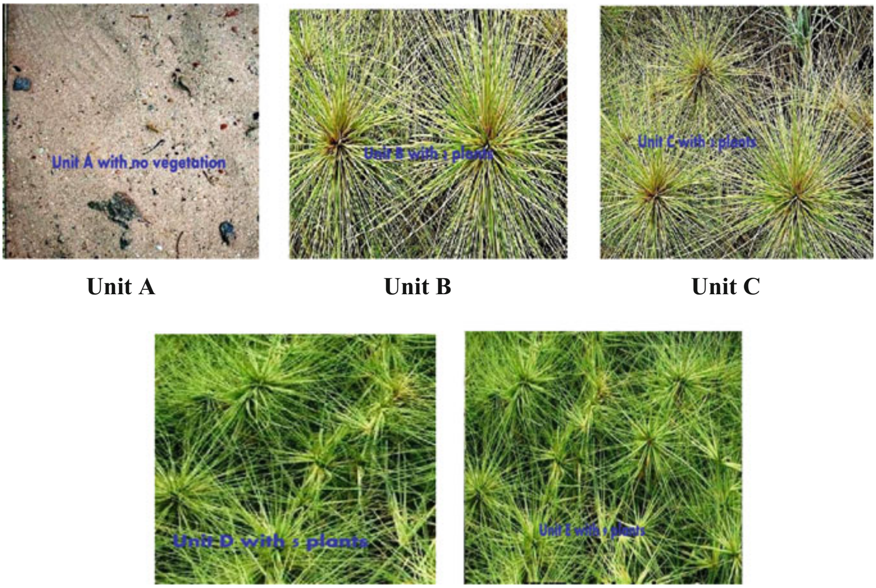
The samples were collected from Kadmath Island of the Lakshadweep archipelago in India.

(b) Collection of samples

Samplings for AGB and BGB estimations of *S. littoreus* were carried out at ebb during March 2016 from the selected station. Samplings were carried out with the aim to observe whether *S. littoreus* can act as a potential sink of carbon considering the vegetation and underlying soil as one single unit of carbon reservoir. Accordingly samples were collected (both the vegetation and underlying soil samples) from five different units with variable biomass owing to different density of the species (Fig. 1).

(c) Biomass estimation of the species

Biomass of the above ground and below ground structures were estimated by uprooting the plants from five quadrates (each of 1 m^2 dimension). Plant materials



Unit A **Unit B** **Unit C**

Unit D **Unit E**

Fig. 1 Five selected units for sampling in Kadmath island, Lakshadweep were thoroughly washed in the ambient water immediately after collection, as well as with tap water, to remove adhering debris and sediments. The vegetative parts were sun dried separately and weighed and the results were expressed as g m^{-2} on an average basis.

(d) Estimation of stored carbon in the vegetative structures

Above ground and below ground parts of *S. littoreus* were dried separately and ground to powder for carbon content analysis using the CHONS analyzer (Flash EA 1112 series, Italy) with a thermal conductivity detector (TCD). The analytical conditions were as follows: Carrier gas—helium carrier gas flow rate—130 ml/min; combustion temperature—900 °C; column temperature—50 °C.

(e) Estimation of Soil Organic Carbon (SOC)

Soil samples were carefully collected from the upper 5 cm of the substratum separately from five different units (A, B, C, D and E) as selected on the basis of vegetation density. In the laboratory, the collected samples were carefully sieved and homogenized to remove roots and other plant and animal debris prior to oven drying to constant weight at 105 °C. Total organic carbon was analyzed by rapid dichromate oxidation method of Walkley and Black (1934).

(f) Analysis of variance (ANOVA)

Analysis of variance (ANOVA) was performed to assess whether biomass and carbon content varied significantly between the five experimental units (as stated in the experimental design). Possibilities less than 0.01 ($p < 0.01$) were considered statistically significant. All statistical calculations were performed using SPSS 14.0 for Windows.

3 Results

Coastal vegetation acts as an important sink of carbon (Mitra et al. 2011; Mitra and Zaman 2014, 2016). The stored carbon in coastal vegetation is a function of biomass, which in turn depends on edaphic factors. Hence results obtained at one place may not be replicated to another site. The present study undertaken in Kadmath Island exhibits more AGB compared to BGB. The ratio BGB:AGB ranges from 1:243.33 to 1:274.63 (Table 1).

Table 1 AGB and BGB in five selected units

Quadrant code (1 m^2 dimension)	Above ground biomass (in g m^{-2})	Below ground biomass (in g m^{-2})	BGB: AGB
A with no plants	0	0	–
B with two plants	80.30	0.33	1:243.33
C with three plants	128.01	0.51	1:251.00
D with five plants	255.41	0.93	1:274.63
E with nine plants	390.85	1.56	1:250.54

Table 2 AGC and BGC in five selected units

Unit	AGC (g C m^{-2})	BGC (g C m^{-2})	BGC:AGC
A with no plants	0	0	
B with two plants	28.24	0.14	1:201.71
C with three plants	45.02	0.21	1:214.38
D with five plants	89.83	0.39	1:230.33
E with nine plants	137.46	0.65	1:211.48

Table 3 SOC percentages in five selected units

Unit	SOC %
A with no plants	0.02
B with two plants	0.04
C with three plants	0.05
D with five plants	0.08
E with nine plants	0.13

AGC and BGC in the species are shown in Table 2. The variations in stored carbon are attributed to variation in number and biomass of the species. The AGC ranged from 28.24 g C m^{-2} to 137.46 g C m^{-2} and the BGC ranged from 0.14 g C m^{-2} to 0.65 g C m^{-2}. The ratio BGC:AGC ranges from 1:201.71 to 1:230.33.

The SOC is shown in Table 3, which is significantly less compared to other coastal regions of Indian subcontinent (Mitra and Zaman 2014, 2016).

4 Discussions

The environment of coastal zone adjacent to Arabian Sea is extremely unfavourable. High temperature along with high salinity and shifting sands has increased the magnitude of hostility in coastal zone. However, few plants species are well adapted to this environment, which are called psammophytes. *Spinifex* sp. is one such grass which belongs to the family Poaceae (Gramineae). It has only one species *S. littoreus* = (*S. squarrosus*) in India. This species functions as a pioneer species and grows in the “foreshore zone” (or pioneer zone) of the supra tidal region, in association with *Ipomoea pes-caprae* = (*I. biloba*). The stored carbon in the species is more in BGB (41.88%) compared to AGB (35.17%) of the species. Accordingly the stored carbon per unit area varies from 28.24 g C m^{-2} to 137.46 g C m^{-2} in AGB and 0.14 g C m^{-2} to 0.65 g C m^{-2} in BGB (Table 2). ANOVA results (Table 4) also indicate that there are significant statistical differences in biomass and stored carbon between units ($p < 0.01$).

The difference in biomass or density of the species has a regulatory role on SOC percentage of the substratum. The SOC exhibited a linear relationship with the biomass of the species, which confirms the contribution of the vegetation in the

Table 4 ANOVA result showing variation of biomass and stored carbon between different vegetative parts and different vegetative layers

Variables	F_{cal}	F_{crit}
Biomass		
Between units	9.33	5.99
Stored carbon		
Between units	9.31	5.99

SOC pool of the substratum. The results demonstrate that with conservation of *S. littoreus*, additional benefits in terms of carbon sequestration (preferably in the AGB) could be achieved without additional investments.

The species *S. littoreus* as such is not very economically important although fisher folk occasionally use it as fuel. Due to its adaptation to extremely harsh environment, the species does not require any special care for its survival and growth. The species has ecological importance as it prevents desertification by retarding the sand particles from moving inland. The stored carbon in the plant particularly in the AGB is another added value in ecosystem services of the species. It is therefore extremely important to conserve the species for protecting the sand dunes, maintaining the beach stability, to retard the process of desertification and increase the potential of carbon sequestration.

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Chapter 7

Assessment of Altitudinal Mediated Changes of CO_2 Sequestration by Trees at Pachamalai Reserve Forest, Tamil Nadu, India

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Abstract Forest plays a significant role in storage of atmospheric carbon dioxide in plants as well as soil. This paper provides an assessment of the potential of tree growth in different altitudes and its contribution in carbon dioxide sequestration in Pachamalai reserve forest in India. The Pachamalai reserve forest is a part of Eastern Ghats in Tamil Nadu. The amount of biomass and carbon stock was estimated by allometric equation at different altitudes. The results revealed that height and diameter of trees are increasing from lower to higher altitudes. Higher altitude trees attained more height and diameter, especially the trees *Tamarindus indica, Ficus benghalensis, Artocarpus heterophyllus, Lepisanthus tetraphyllus, Terminalia paniculata,* and *Tectona grandis*. The presence of total biomass in 15 (10 m × 10 m) quadrats at different altitudes of Pachamalai forest is 1679 tons and it stores 839 tons of carbon. 3081 tCO_2 intake by trees in 15 quadrats, thus indicating that Pachamalai reserved forest had sequestered significant level of carbon dioxide. This study is useful for sustainable management of the Pachamalai reserve forest and can help in reducing the pressure on forest resource while sequestering carbon dioxide from the atmosphere.

Keywords Pachamalai hills · Altitude · Allometric equations · Forest biomass · Carbon stock

Abbreviations

tCO_2	Tons of carbon dioxide
CDM	Clean development mechanisms

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IPCC	Intergovernmental Panel on Climate Change
GtC	Gigatons of carbon
$GtCO_2$	Gigatons of carbon dioxide
AGB	Above ground biomass
BGB	Below-ground biomass
TB	Total biomass
ppm	Parts per million
Mg ha^{-1}	Megagram per hectare
GtC	Gigatones of carbon
PgC	Petagrams of carbon
BA	Basal area
H	Tree height
REDD	Reducing emissions from avoided deforestation and forest degradation

1 Introduction

In recent times, anthropogenic activities are accelerating increase of carbon dioxide (CO_2) emissions in the atmosphere through fossil fuels burning, industrialization and deforestation, resulting in global warming and climate change (Upadhyay et al. 2005). Projections indicate that carbon dioxide level in the atmosphere may increase up to 600 ppm (0.06%) in 2030, twice that of preindustrial era, if no action is taken (Nguyen 2012). Deforestation contributes about 5.9 $GtCO_2$ annually in the world (IPCC 2006). The current rate of deforestation and clearing of tropical forests could release an additional 87–130 Gt of CO_2 to the atmosphere by 2100 (Ross and Sheikh 2010).

In India about 24% of the geographical area is under forest cover, in which tropical forests contribute nearly 83% of the forest area. It is estimated about 53% of the total geographical area of the country is subjected to erosion and land degradation (Singh et al. 2002, 2004; Datta and Agarwal 2003). The increasing level of CO_2 in the atmosphere can be reduced in two ways, (i) controlling emissions and (ii) increasing storage of carbon. Forest ecosystem acts as natural storage for carbon and regulate global climate. The response of forests to the rising atmospheric CO_2 concentrations is crucial for the global carbon cycle as they have huge potential in sequestering and storing more carbon than any other terrestrial ecosystem (Jandl et al. 2007; Ackerman and Sundquist 2008). The Carbon sequestration project at University of California, USA has investigated Giant Sequoias species and its role in climate change abatement. The natural range of Giant Sequoias is a narrow band along the Western slopes of the Sierra Nevada range. The tree grows at high altitudes >1200 m in a total area of 36,000 acres. Having survived for thousands of years, enduring drought, forest fires, and diseases, if these can be propagated genetically and planted, so that the forest is restored at other places, it can help reverse climate change (Jones and O'hara 2011).

David Milarch of Arcangel Ancient Tree Archive has cloned 170 types of trees and grown thousands of trees in different parts of the world, which grow into miniature of 3000 years old tree. These trees are ideal absorber of green house gases with about 1438.892 tons of CO_2 removed by a tree, which is equivalent to 86.7 years of emissions by one person in USA (http://www.dewharvest.com/).

The Intergovernmental Panel on Climate Change (IPCC) identified five carbon pools of the forest ecosystem involving biomass, namely above ground biomass (AGB), below-ground biomass (BGB), dead wood, litter, and soil organic matter (FAO 2005; IPCC 2003, 2006). Photosynthesis transfers CO_2 from the atmosphere and the carbon is stored in wood and other plant tissues (Dilling et al. 2006). As more photosynthesis occurs, more CO_2 is converted into biomass, reducing carbon in the atmosphere and sequestering it in plant tissue above and below ground (Gorte 2009; IPCC 2003) resulting in growth of its different parts (Chavan and Rasal 2010). The biosequestration of carbon can be improved by applying the genetic engineering approaches in plant photosynthesis. It is the way to enhance the capacity of plants to serve as more carbon sinks. Meanwhile, carbon flux in living trees is the largest carbon sequestration which could account for 76–90% of total carbon sequestration in forest ecosystems (Liu et al. 2006). Normally, the rate of sequestrated and stored CO_2 of a given tree is related to the tree size such as stem basal area (BA) and total tree height (*H*) (Tagupa et al. 2010). During the tree growth, BA and *H* should allometrically relate to biomass accumulation and CO_2 stocks of a tree. Different species respond in different ways for carbon utilization (Negi et al. 2003).

Phytosequestration of carbon in growing forests is known to be a cost-effective option for mitigation of global warming. Tree growth may be subjected to environmental gradients associated with elevation, providing convenient scenarios to investigate the potential responses of forest growth (Liang et al. 2010). Carbon storage in tree is beneficial for both environmental and socioeconomic perspectives. The environmental perspective includes the removal of CO_2 from the atmosphere, the improvement of soil quality, and the increase in biodiversity; while socioeconomic benefits include increased yields and monetary incomes from potential carbon trading schemes (McDowell 2002). Under the Kyoto Protocol, United Nations Framework of Convention on Climate Change (UNFCCC) adopted Clean Development Mechanisms (CDM), Joint Implementation and Reducing Emissions from avoided Deforestation and Forest Degradation (REDD) schemes. Storage of carbon in various terrestrial sinks has been proposed as a carbon trading mechanisms (Green et al. 2007; Alamgir and Al-Amin 2007; Chavan and Rasal 2012). REDD + mechanism was ratified during 15th Conference of Parties in Copenhagen 2009 for implementation of Kyoto Protocol. India could have huge potential to promote sustainable management of forests, promote eco conservation and eco earnings, while preventing global warming from reaching tipping point and mitigating climate change (Goel and Das 2012). The aim of this present study is to analyze the growth of trees, the total biomass and amount of carbon dioxide stored by trees at different altitudes, which could potentially identify their role in carbon trading schemes as well.

2 Materials and Methods

2.1 *Study Area*

Pachamalai reserve forest is a part of Eastern Ghats of India. It totally covers a geographical area of 525.23 km^2 and elevation is 1060 m. It lies in the geographical limit of 78° 30″E and 78° 45″E latitude, 11° 10″N and 11° 30″N longitude (Fig. 1). Climate is tropical with temperature ranging between 25 and 30 °C and annual rainfall ranges from 800 to 900 mm. The maximum rainfall is received during the months of September, October, and November through the Northeast monsoon (Panaiyadiyan and Chellaia 2011). It comprises about seven major types of forests namely evergreen forest, semi-evergreen forest, dry evergreen forest, dry-mixed deciduous forest, thorn forest, non-forest area, and wastelands (Selvaraj et al. 2013). According to 2011 census report, the population recorded in and around Pachamalai hill is 231,497. The economic activities of forest dwellers are agriculture, livestock rearing and collection of fuelwood.

2.2 *Estimation of Biomass and Carbon Stock*

In order to estimate the biomass and carbon stock at different altitudes using allometric equation, a field study on tree height (*H*) and diameter (*D*) was carried out. Fifteen 10 × 10 m quadrats in between altitude of 230 to 930 m with 50 m regular interval were laid. The geographical locations of the sampling sites were recorded

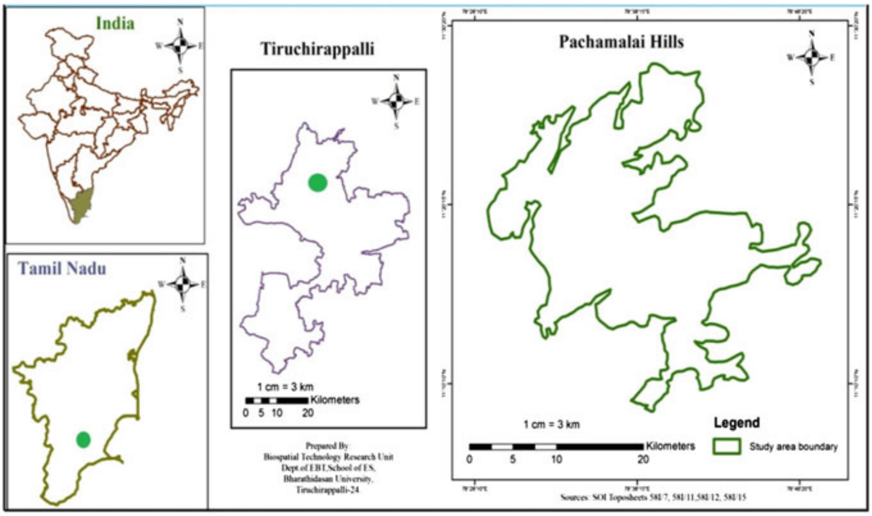

Fig. 1 Location map of the study area

Table 1 Geographical location of sampling sites

Altitude (m)	Lat long
230	78° 37′ 6.899″E; 11° 27 ′25.525″N
280	78° 36′ 34.689″E; 11° 15′ 29.327″N
330	78° 36′ 2.98″E; 11° 26′ 39.486″N
380	78° 34′ 15.832″E; 11° 24′ 10.43″N
430	78° 37′ 15.56″E; 11° 16′ 19.418″N
480	78° 36′ 10.94″E; 11° 26′ 34.236″N
530	78° 40′ 0.689″E; 11° 18′ 39.722″N
580	78° 40′ 53.359″E; 11° 18′ 59.77″N
630	78° 40′ 43.344″E; 11° 17′ 23.201″N
680	78° 37′ 29.066″E; 11° 16′ 28.773″N
730	78° 34′ 36.37″E; 11° 23′ 19.448″N
780	78° 34′ 46.34″E; 11° 16′ 45.041″N
830	78° 41′ 8.825″E; 11° 16′ 56.254″N
880	78° 34′ 42.615″E; 11° 22′ 7.797″N
930	78° 34′ 48.116″E; 11° 21′ 13.104″N

using GPS and represented in the Table 1. The tree height and diameter was measured using clinometer, vernier caliper and measuring tape. AGB includes all living biomass above the soil and BGB consists of live roots and soil (Chavan and Rasal 2011). Generally, for any plant species 50% of its biomass is considered as stored carbon (Brown et al. 2005; Paladinic et al. 2009). Below-ground biomass of tree species was calculated considering 15% of the aboveground biomass (Macdicken 1997). The following allometric equations have been applied for estimation of biomass, amount of carbon stored, the carbon dioxide sequestered in the study area (IPCC 2006; Nguyen 2012; Hangarge et al. 2012; Sheikh et al. 2011).

$$\mathrm{AGB\ (kg)} = 0.0396 \times D^2 \times H^{0.932} \tag{1}$$

$$\mathrm{BGB\ (kg)} = 0.26 \times \mathrm{Above\,ground\,biomass} \tag{2}$$

$$\mathrm{Total\,biomass\ (TB)} = \mathrm{Above\,ground\,biomass} + \mathrm{below\,ground\,biomass} \tag{3}$$

$$\mathrm{Carbon\,storage} = \mathrm{Biomass} \times 50\% \tag{4}$$

$$\mathrm{CO_2} = 3.67 \times \mathrm{C} \tag{5}$$

3 Result and Discussions

Total of 523 trees were measured in 15 quadrats (10 × 10 m) at different altitudes of Pachamalai hills. Those tree species height and diameter was varying according to altitude. The tree height and diameter is increasing from lower altitude to higher altitude. The maximum height and diameter of tree was observed in the altitude 930 m followed by 780, 580, and 880 m altitudes. *Tamarindus indica, Ficus benghalensis*, *Artocarpus heterophyllus, Lepisanthus tetraphyllus, Terminalia paniculata,* and *Tectona grandis* growth was dominant than all other species. These species attained maximum height and diameter and it was observed from 580 to 930 m altitudes (Figs. 2 and 3). The same species was also observed in lower altitudes which attained less height and diameter than higher altitudes. Liang et al. (2010) reported that the radial growth of trees increase along with altitudinal gradients as well as tree-ring width data in comparison to height increment. This variation may be due to climatic factors mainly temperature and rainfall. Temperature decreases with increasing altitude while rainfall increases nonlinearly with altitude in the tropics and hence produces a double complex gradient and affects the tree growth, diversity, and richness along the altitudinal gradient (Brown 1997). The results of this study have revealed a positive relationship between tree growth and altitudes.

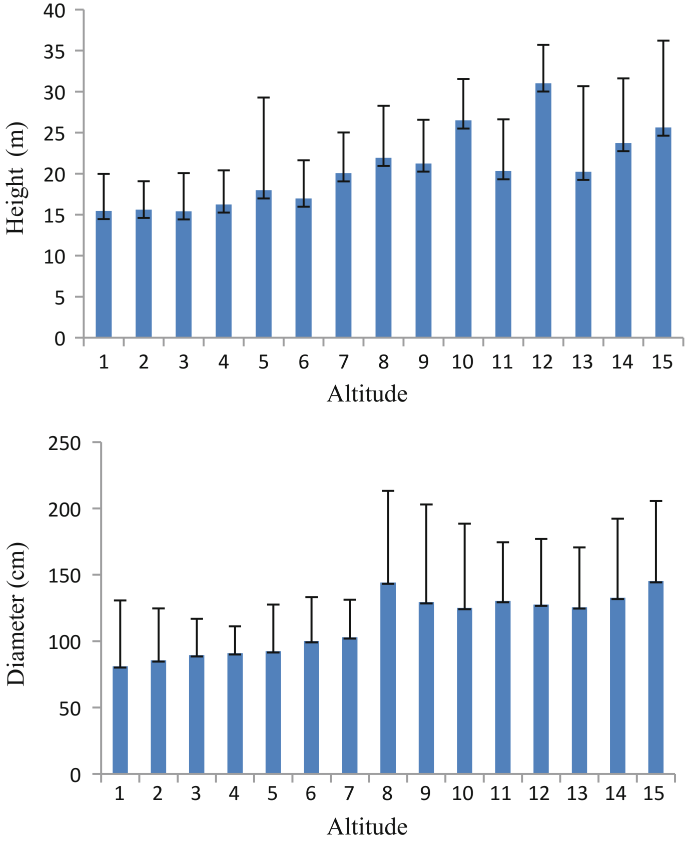

Fig. 2 Mean tree height and diameter in different altitudes

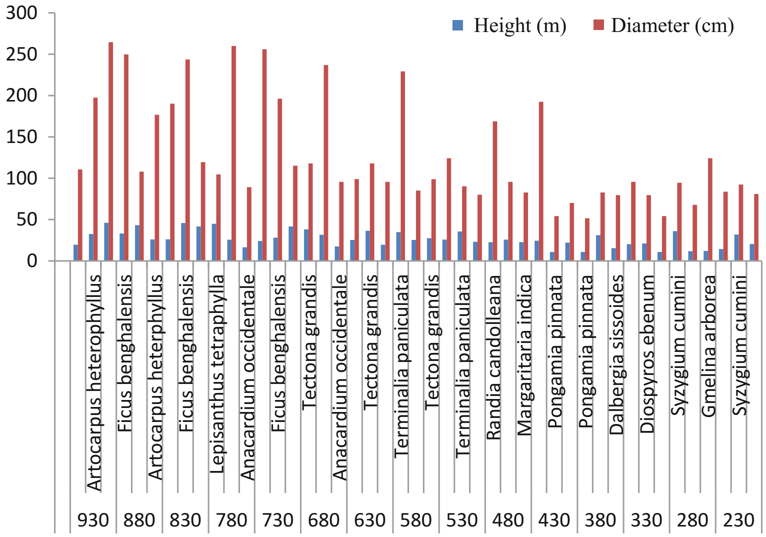

Fig. 3 Dominant species tree height and diameter in different altitudes

The estimation of biomass and carbon stock was carried out by measuring the tree height and diameter. The mean height of tree was observed maximum at 780 m followed by 930 and 880 m altitudes. Maximum mean diameter was experienced at 930 m followed by 580, 880, and 730 m altitudes. The study focuses on altitude wise status of vegetation that has biomass. It was observed that higher altitude contain the highest AGB, below ground biomass and total standing biomass. Maximum AGB was observed in 780 m altitude (15,806 kg) followed by 580 m altitude (14,638 kg) and 880 m (13,342 kg). This altitude (780 and 830 m) has more number of trees than all other altitude. The lowest above-ground biomass was observed in 230 m (3339 kg) followed by 280 m (3752 kg) altitude. These 230 and 280 m altitude trees are less in height and diameter (Table 2). Ensslin et al. (2015) reported that among the different natural habitats, tree biomass was highest at intermediate elevation, shrub biomass declined linearly from 7 Mg ha^{-1} at 900 m to zero above 4000 m and herbaceous biomass was lower at mid-elevations (1 Mg ha^{-1}) in the montane zone. The most AGB accumulation was found in big trees of size class $\geq$80–100 and $\geq$100 cm. Because those trees had the highest stem volume and large diameter, and they also had the lowest number of tree density.

Carbon sequestration potential in different forest types seems to be related to diameter size class. In the tropical rain forest and dry evergreen forest, the main tree size classes that had great potential in carbon sequestering were from small up to medium tree size at $\geq$4.5–20 up to >40–60 cm. On the other hand, the main tree size classes that had the highest potential in carbon sequestration in mixed deciduous forest from small up to medium tree size at >20–40 up to >40–60 cm

Table 2 Estimated total biomass and amount of CO_2 stored in different altitudes

Altitude (m)	Number of trees	Mean height (m)	Mean diameter (cm)	Height	Diameter	AGB	BGB	TAB (kg)	Total biomass (in tons)	Amount of carbon (in tons)	Amount of CO_2 tons
230	25	15.46	81.07	12.83	6572.34	3339.19	667.83	4007.02	40.07	20.03	73.52
280	22	15.61	85.58	12.94	7323.93	3752.95	750.59	4503.54	45.03	22.51	82.63
330	24	15.42	89.47	12.8	8004.88	4057.51	811.5	4869.01	48.69	24.34	89.34
380	24	16.25	91.01	13.44	8282.82	4408.31	881.66	5289.97	52.89	26.44	97.05
430	26	17.99	92.42	14.78	8541.45	4999.2	999.84	5999.04	59.99	29.99	110.08
480	27	16.98	100.11	14	10,022.01	5556.2	1111.24	6667.44	66.67	33.33	122.32
530	26	20.07	103.01	16.36	10,611.06	6874.43	1374.88	8249.31	82.49	41.24	151.36
580	25	21.94	144.19	17.78	20,790.75	14,638.51	2927.7	17,566.2	175.66	87.83	322.33
630	26	21.25	129.49	17.26	16,767.66	11,460.62	2292.12	13,752.7	137.52	68.76	252.34
680	34	26.5	125.05	21.2	15,637.5	13,127.99	2625.59	15,753.6	157.53	78.76	289.06
730	26	20.32	130.26	16.55	16,967.66	11,120.26	2224.05	13,344.3	133.44	66.72	244.86
780	43	31.02	127.51	24.55	16,258.8	15,806.48	3161.29	18,967.8	189.67	94.83	348.04
830	39	20.23	125.6	16.48	15,775.36	10,295.12	2059.02	12,354.1	123.54	61.77	226.69
880	34	23.74	132.68	19.14	17,603.98	13,342.83	2668.56	16,011.4	160.11	80.05	293.8
930	36	25.63	145.24	20.55	21,094.65	17,166.4	3433.28	20,599.7	205.99	102.99	377.99
Total									1679.29	839.59	3081.41

(Terakunpisut et al. 2007). AGB dynamics are an important component of net primary productivity in tropical forests (Clark et al. 2001).

The quantity of biomass at different altitudes of Pachamalai reserved forest is 1679 tons. From this data it is inferred that the total amount of carbon storage is 839 tons and total amount of CO_2 sequestration is 3081 tons (Table 2). Ullah and Amin (2012) reported that natural hill forest of Bangladesh stored total carbon stock was 283.80 tons per hectare (tha^{-1}). The amount of stored carbon stock of Danaba community forest at Oromia regional state of Ethiopia was 507.29 tha^{-1} (Bazezew et al. 2015).

Pachamalai forest tribes depend on forest for agriculture, fuel wood, livestock rearing, etc. The economic value of forest dwellers can be improved by the social implications of carbon forestry projects. Some economists have argued that the conservation of forest ecosystems in the tropics will be difficult unless people are compensated for the environmental services of their forests (Pearce et al. 1996). The costs of carbon sequestration are typically expressed in terms of monetary amounts (dollars) per ton of carbon sequestered: that is, as the ratio of economic inputs to carbon sequestration outputs for a specific program. In general EU companies, paying an average price of $20 per ton of carbon dioxide and Investor Responsibility Research Center prices $28.24 per ton in the year 2012. According to Bloomberg New Energy Financial Report 2013 for Voluntary Carbon Market prices $5.9 per ton of carbon dioxide. Influencing carbon forestry projects could therefore profoundly impact livelihoods. It will encourage the people to protect the forest and environment.

4 Conclusions

The present study revealed that the relationship between growth of trees and altitudes having significant correlation on carbon dioxide sequestration. Maximum height and diameter of trees were attained at higher altitude. The biomass of the forest shows that Pachamalai reserve forests store significant amount of carbon. The total biomass in 15 quadrat of forest was 1679 tons and it sequestered totally 3081 tons of CO_2. This study is helpful to understand the growth of trees at different altitude and its role in mitigating the carbon dioxide level and emphasizes their role in carbon trading schemes. The study gives insights about plants that sequester more carbon dioxide which could be included in the afforestation program and carbon trading schemes. It lays emphasis on improving the conservation of tree species as well as forest ecosystem to mitigate the global climate.

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Chapter 8
Prospects in Mitigating Global Warming by Biomimetic Carbon Sequestration Using Recombinant Microbial Carbonic Anhydrases

T. Satyanarayana and Himadri Bose

Abstract Carbon capture storage and utilization (CCSU) can be a probable and efficient solution for mitigating global warming. It refers to the conversion and storage of CO_2 in stable and usable forms. Carbon sequestration using carbonic anhydrase (CA) has attracted much attention in the recent years. Due to high temperature and CO_2 content in flue gas emitted from coal-based thermal plants, the enzyme for CO_2 sequestration must have thermostability, tolerance to high CO_2 and heavy metals, and alkalistability for mineralization. The extremophilic microbial CAs with these attributes would be useful in sequestering CO_2. The production of large quantities of native carbonic anhydrase from wild microbial strains for carbon capture becomes costly because they possess low levels of CA. The cloning CA-encoding genes from extremophiles and their overexpression in heterologous hosts such as *E. coli* would bring down the cost of enzyme production. Further improvement in the desirable properties of CAs can be achieved through protein engineering approaches. In this chapter, an attempt has been made to review developments in the production of recombinant CAs, their characteristics and applicability in carbon sequestration. Other biotechnological applications of CAs are also briefly discussed.

Keywords Carbonic anhydrase · *E. coli* · Gene cloning · Heterologous expression · Carbon sequestration · Polyextremophilic microbes

Abbreviations

CCSU	Carbon capture storage and utilization
CCS	Carbon capture and storage

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CA	Carbonic anhydrase
GHGs	Green house gases
IPPU	Industrial processes and products use
IPCC	Intergovernmental panel on climate change
CCM	CO_2 concentrating mechanism
NO*x*	Nitrogen oxides
SO*x*	Sulfur oxides
IPTG	Isopropyl β-D-1-thiogalactopyranoside
ArgHCl	Arginine hydrochloride
PU	Polyurethane
MDEA	Methyl diethanolamine
HFM	Hollow fiber membrane
nM	Nanomolar
mM	Millimolar
pM	Picomolar
DMAEMA	*N*,*N*-dimethylaminoethyl methacrylate
PolySFHb-SOD-CAT-CA	Poly stroma-free hemoglobin catalase superoxide dismutase carbonic anhydrase
RuBisCo	Ribulose-1,5-bisphosphate carboxylase/oxygenase
CLM	Control liquid membrane
hCAII	Human carbonic anhydrase II
NCA	*Neisseria. gonorrhoeae*-Carbonic Anhydrase
ECCA	*Escherichia coli* Carbonic Anhydrase
VchCA	*Vibrio cholerae* α-Carbonic Anhydrase
α-CA-HP	A Carbonic Anhydrase *Helicobacter pylori*
β-CA-HP	B Carbonic Anhydrase *Helicobacter pylori*
stCA1	*Salmonella typhimurium* Carbonic Anhydrase 1
stCA2	*Salmonella typhimurium* Carbonic Anhydrase 2
TweCA	*Thalassiosira weissflogii* Carbonic Anhydrase
TwCA1	*Thalassiosira weissflogii* Carbonic Anhydrase 1
PhaCAγ	*Pseudoalteromonas haloplanktis* Carbonic Anhydrase γ
PgiCA	*Porphyromonas gingivalis* Carbonic Anhydrase
mtCA1	*Mycobacterium tuberculosis* Carbonic Anhydrase 1
PCA	*Streptococcus pneumoniae* Carbonic Anhydrase
SSpCA	*Sulfurihydrogenibium yellowstonense* Carbonic Anhydrase
sazCA	*Sulfurihydrogenibium azorense* Carbonic Anhydrase
taCA	*Thermovibrio ammonificans* Carbonic Anhydrase
PCR	Polymerase Chain Reaction
DvCA	*Desulfovibrio vulgaris* Carbonic Anhydrase
PMCA	Persephonella marina EX-H1 Carbonic Anhydrase
SOD	Superoxide dismutase

1 Introduction

One of the severe challenges that we face today is the rise of global average temperature leading to global warming. The earth's temperature has increased by 0.8 °C in the past century. The last century was the warmest among all preceding centuries. This rise in temperature can be easily co-related with increase in the concentrations of green house gases (GHGs) in the atmosphere. Among GHGs, carbon dioxide (CO_2) played a crucial role (Shakun et al. 2012). The concentration of CO_2 in the atmosphere has risen alarmingly since the advent of industrial revolution. The level of CO_2 in atmosphere now is about 398 ppm, as compared to that of 290 ppm before industrial revolution. The main cause of the anthropogenic carbon dioxide emissions are the power plants and industries. They are the major emitters of CO_2 in the form of flue gases. The energy sector in India is responsible for 71% of country's total GHG emissions, as revealed in a report from India to the United Nations on climate change. Agriculture sector emits 18% GHG's (methane and nitrous oxides) followed by Industrial processes and products use (IPPU) sector that accounts for 8 with 3% from waste sector. Along with CO_2, other gases like nitrogen and its oxides, and oxides of sulfur have also played a prominent part in global warming. The composition of flue gas depends on the quality of coal burnt (Solomona et al. 2009).

Today we are leading a very comfortable life mainly because of the modern amenities bestowed upon us. We have never thought of how much our modern life style is contributing to the carbon emissions. This can be calculated in terms of 'carbon footprints'. A carbon footprint is the amount of carbon dioxide (CO_2) we emit individually in any 1-year period. The carbon footprint is made up of two parts, the primary and the secondary: primary footprint is a measure of our direct emissions of CO_2 from burning of fossil fuels including domestic energy consumption and transportation, and the secondary footprint is a measure of indirect CO_2 emissions from the whole life cycle of products we use. Many of our daily activities result in carbon emissions. According to the Cool Climate Network (University of California, Berkeley) consortium, the average U.S. household pumps 49 metric tons of carbon into the atmosphere each year. Similarly if one drives a car over 22 miles every weekday, the annual carbon footprint from commuting is 4.3 metric tons. Even our lavish life style is contributing to the amount of GHG emission (http://timeforchange.org/what-is-a-carbon-footprint-definition).

The increasing carbon emissions are having far-reaching consequences. The first and foremost is the global warming which is leading to climate change. Particularly in the last few decades, there has been a shift in seasonal precipitation rates leading to an adverse affect on hydrological cycles around the globe (5th IPCC report 2014). This has majorly affected the economy of many of the countries which solely depend on seasonal agriculture. Climate-related catastrophes have also direct impact on livelihood of poor people (Adams et al. 1998). Rise in global temperatures have led to increase in sea level due to melting of ice masses. The ocean has absorbed about 30% of the anthropogenic CO_2 emissions leading to its acidification

(26% more as compared to pre-industrial era). Also there has been a shift in the activities and interactions of some of the freshwater and marine species. There has been an abundance and distribution shifts of many phytoplanktons, marine fishes, and invertebrates toward cooler waters, poleward (Houghton 2005). Global warming is proving to be a lethal adversary and it needs to be mitigated. There are talks going on to cut down the carbon emissions using energy sources other than fossil fuels. In a developing country like India, where most of the population resides in villages, we need to consider carbon emissions caused due to the burning of firewood in rural homes. Scientists around the world are trying to devise several strategies for mitigating global warming, besides strengthening the existing ones. Carbon taxation, carbon trading, and emission trading schemes are some of the policies implemented by governments all over the world, which are aimed at mitigating global warming (Princiotta 2007).

Carbon capture and storage (CCS) is evolving as a major advancement in this direction. This term has now been extended to Carbon Capture Storage and Utilization (CCSU), which is defined as 'direct capture of CO_2 from flue gases and other large point sources and its storage in the sites, where it can be reused or stored', so that it will not enter the atmosphere. It can also be described as a climate engineering technique which describes scrubbing of CO_2 from atmospheric air and store it in the underground as mineral carbonates (mineralization). CCS can be broadly divided into physical and biological carbon sequestration. Physical methods of carbon capture are the most predominantly used sequestration methods. It can be also termed as geological sequestration where CO_2 from large point sources (power plants) are initially purified transported into deep underground geological formations and stored in stable form (Orr Jr 2009). This technique heavily depends upon the choice of storage sites. A better storage site can sequester carbon for years without any risk of leakage (Benson et al. 2005). Ocean sequestration is another method of physical carbon sequestration in which CO_2 is either directly pumped into the ocean or sequestered via ocean fertilization. It takes up about two billion metric tons of CO_2 each year (Herzog 1998). Efforts are underway to develop processes for directly converting CO_2 from industrial emissions into useful products (Lim 2015; Faridi and Satayanarayana 2015).

Carbon sequestration can also be carried out using natural means. Afforestation is the best way to sequester CO_2. Trees should be grown for a long time so that carbon can be stored in it for ages (Kindermann et al. 2008). Even as trees die, their biomass can be used to produce biochar and phytoliths (Parr and Sulivan 2005). Modified agricultural practices can also be helpful in sequestering carbon. Practices such as use of cover crops such as grasses and weeds and covering of bare paddocks with hay or dead vegetation may have positive effects on soil, air, and water quality, be beneficial to wildlife and expand food production (Batjes 1996). Production of bioenergy crops is another way by which plants can act as CO_2 sinks. It can also reduce the load on fossil fuels, thereby reducing GHG emissions (Min 2011). Photosynthetic organisms such as *Chlorella* and cyanobacteria can be used directly for sequestration purposes (Kubler et al. 1999). Microorganisms such as methanogens can be used to produce commercial methane from atmospheric carbon via Wood–Ljungdahl pathway for acetate synthesis (Kubler et al. 1999).

Another important biological means for CCS is the use of microbial carbonic anhydrase (CA). It is a ubiquitous enzyme that catalyzes the reversible conversion of CO_2 into bicarbonate. Bicarbonate can be utilized for producing several usable products such as amino acids, limestone, and others. The use of CA as a prospective biocatalyst for CO_2 sequestration has been already established. The current review focuses on production and use of recombinant microbial CAs for CO_2 sequestration.

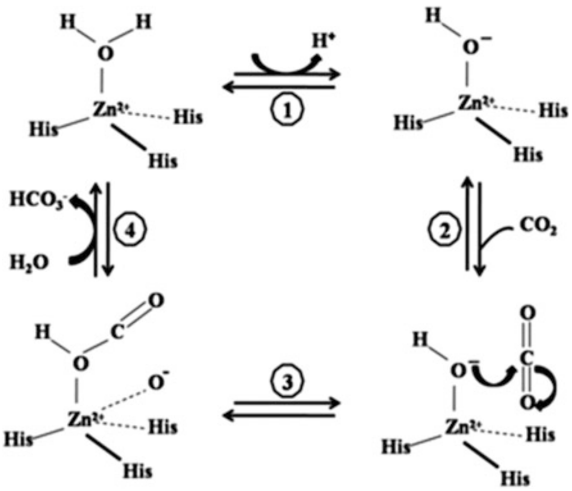
2 Carbonic Anhydrases

Carbonic anhydrases (EC No. 4.2.1.1) are metalloenzymes comprising Zn^{2+} in their active sites. This enzyme has its signature in all three domains of life. It catalyzes the interconversion of carbon dioxide to bicarbonates (Smith and Ferry 2000).

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

This enzyme was discovered in bovine erythrocytes in 1933 (Meldrum and Roughton 1933; Stadie and O'Brien 1933). It is an essential enzyme for CO_2 metabolism in living beings. In mammals, it helps in maintaining acid–base balance, ion transport, and respiration. In plants, it aids in photosynthesis in chloroplasts. It also helps in raising the concentration of CO_2 within the chloroplast in order to increase the carboxylation rate of ribulose 1,5-bisphosphate carboxylase (RuBisCO) (Smith and Ferry 2000). In cyanobacteria and microalgae, CAs are involved in the CO_2 concentrating mechanism (CCM), thereby helping the cells to photosynthesize in the absence of inorganic carbon (Badger and Price 2003). The k_{cat} value of this enzyme is in the order of 10^6 s^{-1} and catalytic efficiency is in the order of 10^8 M^{-1} s^{-1}, making it one of the fastest known enzymes. Six distinct classes have been discovered till now (α, β, γ, δ, ζ and η). It is a classical case of convergent evolution as no sequence similarity is found among all classes. The first CA discovered was that of alpha type. Later many isoforms of this class were also found to be localized in other mammalian tissues. The first prokaryotic CA (which was also of α type) was isolated and characterized from *Neisseria gonorrhoeae* (Veitch and Blankenship 1963). The next type (β-CA) was discovered in plants. Later it was also found in the bacteria and archaea. This type of CA is the most widely spread among all the life forms (Smith et al. 2000). The γ-CA was discovered in hyperthermophilic archaeon *Methanosarcina* (Alber and Ferry 1994). This CA has been found to be associated mainly with archaeal domain. Till date most of the β- and γ-CAs have been characterized from plants and prokaryotic genera. δ-, ζ-, and η-CAs have been isolated from cyanobacteria, marine diatoms, and some dinoflagellates (Xu et al. 2008; Lapointe et al. 2008; Lane and Morel 2000; Del Prete et al. 2014). The use of CA to capture CO_2 from industrial effluents

Fig. 1 Catalytic mechanism of carbonic anhydrases



and at the same time converting the captured CO_2 into mineral carbonates can provide an onsite approach to sequester CO_2 directly from flue gas without its separation from other gases and also do not require compression, making the entire process economical, greener, and safer.

2.1 Catalytic Mechanism

Catalytic mechanism of CA was extensively studied using α-carbonic anhydrases. Interconversion of CO_2 to bicarbonate is a two-step process. In the first step, a fourth histidine near the water molecule accepts a proton (H^+) which is released from the water molecule leaving only hydroxide ion bound to zinc ion. The active site has precise pockets for binding CO_2, which helps in the attachment of substrate to the hydroxide ion. The next step is nucleophilic attack on the carbonyl group by the zinc-bound hydroxide leading to the formation of HCO_3^-. This is the rate-limiting step. The enzyme is then regenerated and the bicarbonate ion is released (Fig. 1) (Lindskog and Joseph 1973; Steiner et al. 1975; Silverman and Lindskog 1988).

3 Problems in Producing Large Quantities of Native Microbial Carbonic Anhydrases

In order to use this enzyme for carbon sequestration, three points are important. First, it should be thermostable so that it can withstand the high temperature of flue gas. Second, for mineralization reaction to take place continuously, alkaline condition is required, thus, enzyme must be alkalitolerant/alkalistable. Also it should be stable and active in the presence of wide variety of flue gas contaminants such as NO*x*, SO*x*, and others. Third, enzyme must be produced in high titres so that it can be used for carbon sequestration. To produce the enzyme in high titres, production optimization has to be carried out by different approaches and a very high production must be achieved. This optimization process is labor intensive and it adds to the cost as well as time of production. Initially there were studies on the sequestration efficiency using human carbonic anhydrase (hCAII), although it showed promising results, this was not stable above 50 °C (Mirjafri et al. 2007; Capasso et al. 2012). Even the mesophilic counterparts from prokaryotes (Prabhu et al. 2011; Ramanan et al. 2009) showed good CO_2 hydration activity, but again thermostability and alkalistability were the important aspects which were not achieved in CAs from mesophiles. Improvement in stabilities (thermal and alkali) can be carried out either by immobilization techniques or by molecular approaches, which add to the production cost (Prabhu et al. 2009; Fisher et al. 2012; Daigle and Desrochers 2009). Enzymes from microorganisms which can survive in environmental extreme stresses would be expected to solve this problem (Daigle et al. 2015).

During the second half of twentieth century, many life forms have been discovered which are able to survive in extreme environmental conditions (Mesbah and Wiegel 2012) such as high/low temperatures (thermophiles and psychrophiles), pH (alkaliphiles and acidophiles), pressure (barophiles), and others. These organisms prove to be useful in bioprospecting (Kumar and Satyanarayana 2011; Dahlberg et al. 1993; Anand et al. 2013). A wide array of products can be produced from them including enzymes, antibiotics, biofuels, antioxidants, and several others. The main advantages of these products lie in the fact that they retain their activities under extreme conditions (Canganella and Wiegel 2011). Many archaeal life forms were also discovered (Mesbah and Wiegel 2012; Alber and Ferry 1994), which need specialized growth conditions. The advent of techniques such as genome mining and metagenomics has led to the discovery of many nonculturable life forms; the genomes of these life forms are also a rich source of products for human welfare (Seckbach et al. 2013).

In order to overcome the problems associated with the cultivation and production of large amounts of products such as enzymes, several attempts have been made to clone the encoding genes and overexpress them in prokaryotic (*E. coli*, *Bacillus subtilis*) as well as eukaryotic (*Pichia pastoris*) hosts. Even CA genes from extremely thermophilic and alkaliphilic nonculturable organisms can be identified using bioinformatic tools, which can be cloned and overexpressed heterologously, thereby producing them in large amounts. The recombinant enzymes expressed in *E. coli* can be very easily purified in one step by Nickel-affinity chromatography as the protein is tagged with amino acid Histidine, thereby simplifying the purification process (Swartz 2001).

4 Attempts in Cloning and Overexpression of Microbial Carbonic Anhydrases

First prokaryotic CA gene to be cloned and heterologously expressed in *E. coli* was α-CA from *Neisseria gonorrhoeae*. The entire gene was cloned and found to encode a protein of 252 residues having a molecular mass of 28.1 kDa. This carbonic anhydrase was heterologously produced in *E. coli* as a periplasmic protein lacking the N terminal 26 residues, suggesting that the *E. coli* processing machinery recognized this fragment as a signal sequence and cleaved it (Chirica et al. 1997; Jo et al. 2013). Its crystal structure was solved to a resolution of 1.78 Å with human carbon anhydrase (hCAII) as a template. The major secondary structure is a 10-stranded, twisted β-sheet that divides the molecule into two halves. The α-sheet is antiparallel with the exception of two pairs of parallel strands. Its structure was more or less found to be similar to hCAII with a few exceptions (Huang et al. 1998). Recombinant truncated (without signal peptide) *N. gonorrhoeae*-CA (NCA) was highly expressed and purified at the 63% yield. The yield of recombinant NCA in the soluble fraction was ~ 106 mg L^{-1} with a specific activity of 3090 U mg^{-s}in the pure protein (Kim et al. 2012).

In *E. coli*, a CA of β-type was discovered as the gene (*cynT*) encoding this enzyme has homology with that of spinach and pea β-CA. This was one of the earliest known β-type CA to be discovered. It is induced in the presence of cyanate as the gene (*cynT*), which is a part of cyanase operon (Sung and Fuchs 1988). Another β-CA homolog was discovered in *E. coli*, when its genome was sequenced. It was designated as *cynT2* having 30% homology with that of *cynT* (Fujitha et al. 1994). The protein was designated as ECCA. The gene encoding this enzyme was cloned and heterologously expressed in *E. coli*. Crystal structure of ECCA was solved to a resolution of 2.0 Å and it was found to be a tetramer with each monomer consisting of a central four-stranded parallel β-sheet which is flanked on one side by five major α-helical segments. Its active site consists of a Zn^{2+} atom coordinated by one histidine (His98), two cysteine (Cys42 and Cys101), and one aspartate (Asp44) residues in a tetrahedral arrangement. The aspartate makes contact with the metal and water molecule, which is away from the active site. Its secondary structure comprised four strands of parallel β sheets flanked with five α-helical segments (Cronk et al. 2001).

All CA-encoding genes (*can*, *cynT*, *caiE*, *pay*, and *yrdA*) from *E. coli* have been cloned and overexpressed and their expression profiles have been studied in response to different growth conditions (Merlin et al. 2003). In *Anaebena*, the gene-encoding α-CA *ecaA* was cloned in *E. coli*; there was no detectable CA activity, but antisera against CA cross-reacted with a protein of 29 kDa in the whole cell lysate (Soltes-Rak et al. 1997). *Synechococcus* harbors multiple CA genes (*ccaA, isfA* etc.), which have close homology with *cynT* of *E. coli*. Even gene-encoding γ-CA was also identified and expressed heterologously, but activity was not detected (So and Espie 1998). A gene that encodes β-CA was identified in *Methanobacterium thermoautotrophicum*; this was expressed in *E. coli* as a thermostable enzyme (Smith et al. 2000). This enzyme known as CabCA was the first β-CA to be characterized from the archaeal domain. Its crystal structure was solved and it showed that CabCA is a dimer with a subunit fold as that of 'plant'-type β-class carbonic anhydrase. CA from *Neisseria gonorrhoeae* (*ng*CA) was expressed in the periplasm of *E. coli*, thereby generating a bacterial whole cell catalyst. It was expressed in soluble form with high thermal stability (Jo et al. 2013). A γ CA gene from *Serratia* sp. was heterologously cloned and expressed in *E. coli*. The recombinant purified enzyme yield was about 38 mg/L (Srivastava et al. 2015). Carbonic anhydrase was also cloned and expressed from many pathogens to understand its role in pathogenesis. *Vibrio cholerae* α-CA (VchCA) was cloned and heterologously expressed in *E. coli* while searching for novel proteins involved in the virulence/survival of the bacterium and to find new target for drugs. Translated genome inspection of this organism led to discovery of three putative CA genes (α, β, γ) which may have a role in its pathogenesis (Del Prete et al. 2012). Similarly, CAs from other pathogens such as *Leishmania*, *Brucella*, *Helicobacter pylori*, *Salmonella,* and others were also cloned to study their possible role in bacterial pathogenesis (Table 1).

Alpha CA from *Helicobacter pylori* was cloned and expressed in *E. coli* and the yield was approximately 30 mg/L of bacterial culture. Kinetic parameters for CO_2 hydration catalyzed by the *H. pylori* enzyme at pH 8.9 and 25 °C ($k_{cat} = 2.4 \times 10^5\ s^{-1}$, $K_m = 17$ mM, and $k_{cat}/K_m = 1.4 \times 10^7\ M^{-1}\ s^{-1}$) (Chirica et al. 2001). *H. pylori* also encodes a periplasmic α-CA (α-CA-HP) and a cytoplasmic β-CA (β-CA-HP) (Bury-Mone et al. 2008). The CA is active over broad salinity range of 0–4 M NaCl. A putative γ-CA encoding gene of *Azospirillum brasilense* was cloned and overexpressed in *E. coli* (Kaur et al. 2009). Its expression was induced in the presence of high CO_2 in stationary phase. A full-length open reading frame of marine diatom encoding a δ CA gene from *Thalassiosira weissflogii* has been cloned and functionally expressed in *E. coli* using pTWIN2 expression vector (Lee et al. 2013). Some of the thermostable carbonic anhydrases from hyperthermophilic organisms such as *Methanobacterium thermoautotrophicum*, *Sulfurihydrogenibium*, *Thermovibrio ammonificans,* and others have been cloned and heterologously expressed in *E. coli* (Table 1). CAs from these organisms were cloned for studying their utilization in mitigating global warming. CAs from these thermophilic bacteria were found to be extremely thermostable and they displayed very promising results in CCS. These enzymes have a potential to become a promising candidate for sequestering CO_2 from flue gases (Capasso et al. 2012).

Table 1 Reports of cloning, expression, and characteristic features of bacterial carbonic anhydrases

Sl. No.	Organism	Type of CAs	Cloning host/vector	Molecular weight	Other features	Reference
1	*Neisseria gonorrhoeae*	α (ngCA) NCA (without signal peptide)	*E. coli* [pACA1, pET-22b(+), pETat]	25.31 kDa	$k_{cat} = 1.1 \times 10^6$ s^{-1} $K_m = 20$ mM at pH 9.25 °C, also highly expressed in the periplasm of *E. coli* to generate whole cell biocatalyst	Chirica et al. (1997), Jo et al. (2013), Kim et al. (2012)
2	*E. coli*	B (ECCA)	*E. coli* (pET-3a)	27 kDa	Tetramer	Cronk et al. (2001)
3	*Anaebena*	α	*E. coli*	29 kDa	Not active	Soltes-Rak et al. (1997)
4	*Synechocystis PCC6803*	γ	*E. coli*	–	Not active	So and Espie (1998)
5	*Methanobacterium thermoautotrophicum*	β (CabCA)	*E. coli* (pET16b)	21 kDa	$k_{cat} = 1.7^3 \times 10^4$s^{-1} $k_m = 2.9$ mM at pH 8.5 Optimal CO$_2$ hydration activity at 75 ° C, Tetramer	Smith et al. (2000)
6	*Serratia* sp.	γ	*E. coli* pET21b(+)	29 kDa	$k_m = 12$ mM, $V_{max} = 5.2 \times 10^{-4}$ µM min^{-1} $k_{cat} = 7.1 \times 10_4$ s^{-1} stable in alkaline range (7.6–10)	Srivastava et al. (2015)
7	*Vibrio cholerae*	α (hpαCA)	*E. coli* (pET15b)	26.4 kDa	$K_m = 11.7$ mM $k_{cat} = 8.23x10^5$s^{-1} $k_{cat}/K_m = 7.0 \times 10^7$ M^{-1} s^{-1}	Del Prete et al. (2012)
9	*Brucella suis*	β	*E. coli* (pET15b)	25 kDa	$k_{cat} = 1.1 \times 10^6$, $k_{cat}/K_m = 8.9 \times 10^7$ M^{-1} s^{-1} Inhibition constants in presence of sulfonamides 7.3–8.56 nM	Joseph et al. (2010)
10	*Helicobacter pylori*	α	*E. coli* (pACA1)	28.28 kDA	k$_{cat} = 2.4 \times 10^5$s^{-1} km = 17 mM $k_{cat}/K_m = 1.4 \times 10^7$ M^{-1} s^{-1} at pH 8.9 and 25 °C	Chirica et al. (2001)

(continued)

Table 1 (continued)

Sl. No.	Organism	Type of CAs	Cloning host/vector	Molecular weight	Other features	Reference
11	*Salmonella typhimurium*	β (two stCA1 and stCA2)	*E. coli* (pGEX-4T2)	24.8 kDa (stCA1) 26.6 kDa (stCA2)	$k_{cat} = 0.79 \times 10^6\ s^{-1}$ and $1.0 \times 10^6\ s^{-1}$ $k_{cat}/K_m = 5.2 \times 10^7\ M^{-1}\ s^{-1}$ and $8.3 \times 10^7\ M^{-1}\ s^{-1}$	Vullo et al. (2011)
12	*Azospirillum brasilense*	β	*E. coli* (pET15b)	26 kDa	Growing at elevated levels CO_2	Kaur et al. (2009)
13	*Thalassiosira weissflogii*	δ (TweCA)	*E. coli* (pET15b)	32.3 kDa	$k_{cat} = 1.3 \times 10^5\ s^{-1}$ $k_{cat}/K_m = 3.3 \times 10^7\ M^{-1}\ s^{-1}$	Del Prete et al. (2014)
14	*Thalassiosira weissflogii*	δ (TwCA1)	*E. coli* (pTWIN2)	59 kDa	Possess both CO_2 hydration and esterase activity	Lee et al. (2013)
15	*Sulfurihydrogenibium azorense*	α	*E. coli* (pET15b)	26 kDa	$k_{cat} = 4.40 \times 10^6$ $k_{cat}/K_m = 3.5 \times 10^8\ M^{-1}\ s^{-1}$ stable at 90–100 °C for several hours, alkalistable (pH 9.6)	De Luca et al. (2013)
16	*Sulfurihydrogenibium yellowstonense* YO3AOP1	α	*E. coli* (pET15b)	26.1 kDa	$K_m = 26$ mM $V_{max} = 7100$ mM (using CO_2) as substrate Stable at 100 °C for 2 h, alkalistable (pH 9.6)	Capasso et al. (2012)
17	*Thermovibrio ammonificans*	α	*E. coli* [pET-22b(+)]	23 kDa	$k_{cat}/K_m = 1.6 \times 10^8$ Tetramer, Highly thermostable, Half-life of 77 days at 60 °C	Jo et al. (2014)
18	*Persephonella marina*	α	*E. coli* [pET42b, pET-22b(+)]	23 kDa	$k_{cat}/K_m = 3.0 \times 10^7$ Dimer, half-life at 100 °C was 88 min ($T_m = 84.5$ °C)	Jo et al. (2014), Kanth et al. (2014)
20	*Bacillus mucilaginosus*	Five (CA0, 1, 2, 3, 4)	*E. coli* pET30a (+)	25 kDa to 55 kDa	NA	Xiao et al. (2014)

(continued)

Table 1 (continued)

Sl. No.	Organism	Type of CAs	Cloning host/vector	Molecular weight	Other features	Reference
21	*Methanosarcina thermophila*	γ	*E. coli* pUC18	84 kDa (native molecular mass)	Optimal Activity at 55 °C Stable at 75 °C for 15 min, Activity doubles on replacing zinc with cobalt	Albert and Ferry (1994)
22	*Methanosarcina thermophila*	γ (Mt Cam)	*E. coli* pET22b	62 kDa (native molecular mass)	$K_m = 3.0$ mM $k_{cat}/K_m = 1.7 \times 10^{-6}$ $M^{-1}\ s^{-1}$	MacAuley et al. (2009)
24	*Pyrococcus horikoshii*	γ PhCamH	*E. coli*	NA	NA	Jeyakanthan et al. (2008)
26	*Hahella chejuensis*	α	*E. coli* pETDuet-1	25 kDa	Alkalistable, halophilic enzyme also retains its activity at broad pH ranges (pH 6.0–10.0)	Ki et al. (2013)
27	*Enterobacter* sp. B13	β (B13-CA)	*E. coli* pET-15b	25 kDa	$k_{cat} = 4.8 \times 10^5 s^{-1}$ $k_{cat}/K_m = 5.6 \times 10^7\ M^{-1} s^{-1}$	Eminoğlu et al. (2015)
28	*Pseudoalteromonas haloplanktis*	γ (PhaCAγ)	*E. coli* pET-15b	NA	$k_{cat} = 1.4 \times 10^5\ s^{-1}$ $k_{cat}/K_m = 1.9 \times 10^6\ M^{-1}\ s^{-1}$ K_I (acetazolamide) = 403 nM	De Luca et al. (2015)
29	*Porphyromonas gingivalis*	γ (PgiCA)	*E. coli* pET-15b	21 kDa (65 kDa native molecular weight)	$k_{cat} = 4.1 \times 10^5\ s^{-1}$ $k_{cat}/K_m = 5.4 \times 10^7\ M^{-1}\ s^{-1}$ K_I (acetazolamide) = 324 nM	Del Prete et al. (2014)
30	*Mycobacterium tuberculosis*	β (mtCA1)	*E. coli* pGEX-4T2	NA	$k_{cat} = 3.9 \times 10^5\ s^{-1}$ $k_{cat}/K_m = 3.7 \times 10^7\ M^{-1}\ s^{-1}$ K_I (Sulfonamide derivatives) = 1–10 μM	Minakuchi et al. (2009)

(continued)

Table 1 (continued)

Sl. No.	Organism	Type of CAs	Cloning host/vector	Molecular weight	Other features	Reference
31	*Rhodopseudomonas palustris*	α	*E. coli* pMG103	27 kDa	Dimer Native molecular weight = 54 kDa	Puskás et al. (2000)
32	*Streptococcus pneumoniae*	β (PCA)	*E. coli*		$k_{cat} = 7.4 \times 10^5\ s^{-1}$ $k_{cat}/K_m = 6.5 \times 10^7\ M^{-1}\ s^{-1}$ at an optimum pH of 8.4 Inhibition constant(K_Is) in presence of inorganic anions (Cl^-, Br^-) = 21–98 μM)	Burghout et al. (2011)

5 Problems Encountered in Cloning and Heterologous Expression of Microbial CAs

The most common bottleneck in cloning and expression of genes in prokaryotes is in obtaining the enzyme in soluble and active form. In *Anaebena* the gene-encoding alpha CA *ecaA* was cloned in *E. coli*; there was expression, but CA activity was not detected (Soltes-Rak et al. 1997). Gene-encoding gamma CA was identified in *Synechococcus* and expressed heterologously, but the activity was not detected (So and Espie 1998). Many a time expression of recombinant proteins in *E. coli* result in the formation of inclusion bodies, where most of the proteins get aggregated into nonnative confirmations, thus, they have to be extracted/solubilized from the inclusion bodies (Clark 2001). Optimization of IPTG concentration, growth temperature after induction (with IPTG), and incubation time after induction may lead to successful expression of recombinant proteins (Prasad et al. 2011). If the problem persists, other strategies are used.

Techniques such as dialysis and dilution are used to obtain the proteins in soluble native confirmations. Although refolding is achieved, it consumes a lot of time and often the protein is rendered inactive during the refolding process due to the reformation of aggregates and in the presence of other misfolded species (Marston 1986; Tsumoto et al. 2003; Umetsu et al. 2003). Use of chemical denaturants and additives ably assist in protein refolding. These can be divided into three types: denaturants, protein stabilizers, and protein aggregation inhibitors. Urea and guanidine-HCl are typical denaturants which denature by chaotropic effect at high protein concentration (Hevehan and Clark 1997; Orsini and Goldberg 1978; Yamaguchi et al. 2013). Protein stabilizers such as amino acids (arginine) and their derivatives (ArgHCl) aid in refolding processes by decreasing protein aggregation. Many protein aggregation inhibitors (glycerol, polyethylene glycol) have also been used, which assist in protein refolding (Kudou et al. 2011; Ohtake et al. 2011). Other methods have been reported for refolding of inactive protein into an active confirmation namely, size-exclusion chromatography (Li et al. 2004), reversed micelle systems (Sakono et al. 2004), zeolite absorbing systems (Nara et al. 2009), the natural GroEL-GroES chaperone system (Zhi et al. 1992), and use of laminar flow in microfluidic chips (Jahn et al. 2007). Some of the other problems associated with heterologous protein expression in prokaryotes such as *E. coli* include the absence of posttranslational modifications (N&O-glycosylations), seldom proteolytic cleavage, and disulfide bond formations (Sahdev et al. 2008). Davis et al. (1999) proposed a rational strategy for the use of possible fusion partners that could bestow solubility to proteins expressed in *E. coli*. Possible fusion partners were identified using a statistical solubility model. Proteins predicted to be highly soluble were fused to the recombinant proteins to increase their solubility.

Another problem that may arise during cloning is codon bias. Codon usage bias refers to differences in the frequency of occurrence of synonymous codons in coding DNA. Different organisms often show particular preferences for one of the several codons that encode the same amino acid (a greater frequency of one will be found than expected by chance). During synthesis of the recombinant protein, depletion of low-abundance tRNAs occurs. This deficiency may lead to amino acid misincorporation and/or truncation of the polypeptide, thus affecting the heterologous protein expression levels (which will be low at best) and/or its activity. Due to this, the successful expression of recombinant proteins at times becomes difficult in other heterologous hosts' such as *E. coli* and *Pichia pastoris* (Gustafsson et al. 2004). Optimal codons in fast-growing microorganisms like *E. coli* or *Saccharomyces cerevisiae* help in achieving faster translation rates and high accuracy. A codon-optimized α-carbonic anhydrase from *Dunaliella* species was successfully expressed in *E. coli* and was used for CO_2 sequestration applications (Kanth et al. 2012). In another study, synthetic gene based on *Escherichia coli* codon usage of a new α-type CA (HC-aCA) of *Hahella chejuensis*, a marine microorganism, was highly expressed in *E. coli* (Ki et al. 2013). The codon-optimized carbonic anhydrase gene of thermophilic *Persephonella marina* EX-H1 (PMCA) was expressed and characterized. The gene was cloned after removal of signal peptide; five times more activity was observed than that of the intact gene (Kanth et al. 2014). Researchers have modified human carbonic anhydrase II (hCAII) by altering some of its surface amino acid residues to make it thermostable. Six surface amino acid residues Leu100, Leu224, Leu240, Tyr7, Asn62, and Asn67 were replaced by His, Ser, Pro, Phe, Leu, and Gln, respectively, by mutagenesis. These mutations on the surface amino acids increased the number of H bonds and also enhanced its hydrophilicity, besides increasing thermostability by 6 °C (Fisher et al. 2012).

6 Applicability of Recombinant CAs in Carbon Sequestration

Initially the use of carbonic anhydrase as a potential sequestering agent proved to be highly effective (Mirjafri et al. 2007). Later many researchers used bacterial sources for obtaining carbonic anhydrases for sequestration purposes. Many bacterial CA genes were cloned and the recombinant CAs have been used for sequestration purpose. Recombinant CA without signal peptide from *Neisseria gonorrhoeae* (NCA) was highly expressed in soluble form in *E. coli*; its ability to accelerate the formation of calcite crystals was studied (Kim et al. 2012). Many CA genes from thermophilic and mesophilic microbial sources were expressed in *E. coli* and the recombinant CAs were used for carbon sequestration. Fan et al. (2011) had successfully cloned and expressed α-CA from *Helicobacter pylori* on the outer membrane of *E. coli* by surface-anchoring system taken from ice nucleation protein from *Pseudomonas syringae*. CO_2 sequestration using whole cells of *E. coli* having CA on its surface was carried out and its effectiveness in a CLM device was also checked. CA-displaying *E. coli* cells have been used in CLM for CO_2 sequestration with an increased stability for at least 3 days. The recombinant enzyme SspCA from the thermophile *Sulfurhydrogenibium* sp. was applied as a potential biocatalyst for CO_2 capture processes based on regenerative absorption into alkaline solutions (Russo et al. 2013). This enzyme was also found to be active even after 48 h of incubation at 100 °C, when immobilized in polyurethane (PU) foam (Capasso et al. 2012). A bioreactor which contained 'PU-immobilized enzyme' (PU-SspCA) as shredded foam was used for experimental tests aimed at verifying the CO_2 capture capability in the conditions that mimic the power plants (Fig. 2). In this bioreactor, a gas phase containing CO_2 was placed in contact with a liquid phase under the conditions, where CO_2 could be easily absorbed and efficiently converted into bicarbonate by the α-CA (Migliardini et al. 2014).

The SazCA from the thermophilic bacterium *Sulfurihydrogenibium azorense* is the fastest known CA till date with k_{cat}/K_m value of $3.5 \times 10^8\ M^{-1}\ s^{-1}$ (De Luca et al. 2013). It is highly thermo-alkali-stable and retains its carbon dioxide hydration activity even after incubation at 80 and 90 °C for several hours at pH 9.6. In order to operate bioreactors for sequestering carbon from flue gas, CAs must be also

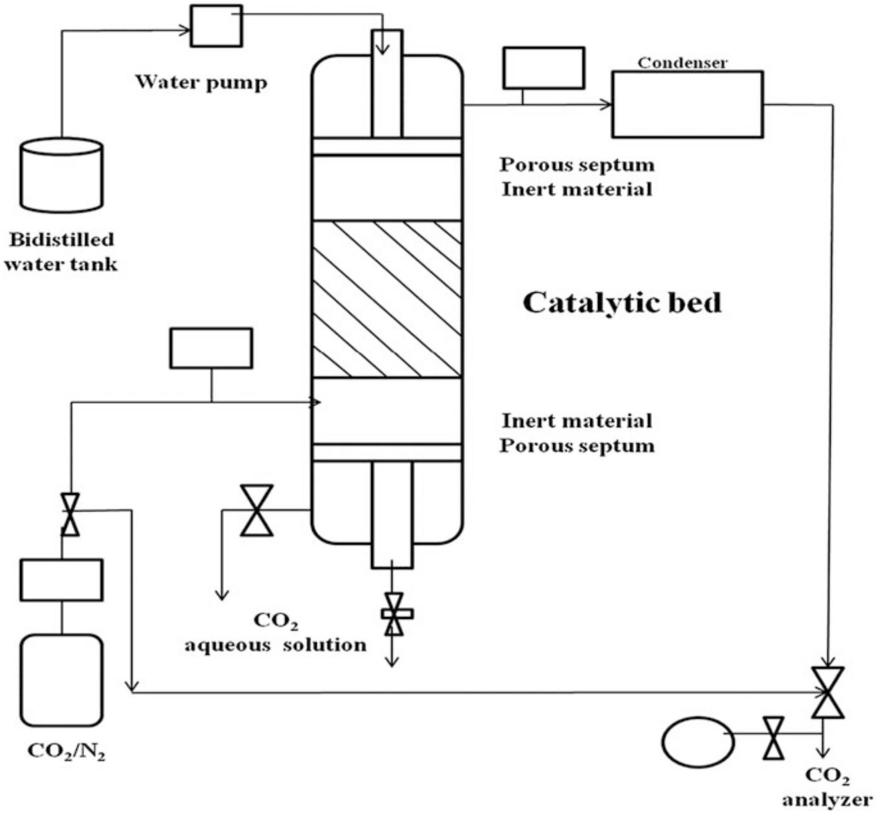


Fig. 2 Scheme of the experimental apparatus used for CO_2 biomimetic absorption tests by three-phase trickle-bed reactor (adapted from Migliardini et al. 2014)

tolerant to the oxides of nitrogen and sulfur. Ssp CA and Saz CA retain activity in the presence of various anionic inhibitors such as NO^{2-}, NO^{3-}, and SO_4^{2-} and high concentration of carbonates, bicarbonates, and hydrogen sulfides (De Luca et al. 2012; Vullo et al. 2012). These properties make them efficient candidates for carbon sequestration. Recombinant alkalistable α-CA from *Serratia* sp. was also successfully employed in forming calcite crystals (Srivastava et al. 2015). A-CAs from *Persephonella marina* and *Thermovibrio ammonificans* (thermophilic Gram-negative bacteria) were also expressed in *E. coli*; these successfully accelerated CO_2 sequestration. Well-defined calcite crystals were formed in the presence of enzyme (Jo et al. 2014). CA from *Thermovibrio ammonificans* (taCA) is much more thermostable than SazCA and SspCA with half-life of 77 days at 60 °C. CA gene was cloned and expressed from *Bacillus mucilaginosus* and the effects of recombinant protein on wollastonite dissolution and carbonate formation under varied CO_2 conditions were explored. Correlation between CA gene expression and sufficiency or deficiency in calcium and CO_2 concentration was studied using real-time PCR. The findings confirmed that the effects of CA and CO_2 concentration were negatively correlated. Further, the report suggested that role of microbial CA in silicate weathering increased (Xiao et al. 2014). Kanth et al. (2012) used recombinant α-type CA from *Dunaliella* sp. and used it in the conversion of CO_2 to calcite and the enzyme efficiently catalyzed the mineralization of CO_2 to $CaCO_3$ and produced 8.9 mg of calcite per 100 μg (172 U/mg) enzyme in the presence of 10 mM Ca^{2+}.

The hCAII has been modified for increasing its thermostability. Its proton transfer rate increased sixfold (Fisher et al. 2012). As per US patent no. 7521217 filed by CO_2 solutions, some other mutations that contributed to increased thermal stability are Ala65Thr, Phe93Leu, Gln136His/Tyr, Lys153Asn, Leu198Met, and Ala247Thr. CO_2 Solutions Inc. utilizes this CA as an onsite scrubber for separation of carbon from flue gases (CO_2 Solutions Inc. 2012). This technology has increased the carbon adsorption rate 40 times as compared to the previous technologies. Alvizo et al. (2014) proposed a method in which flue gas was transferred to an absorber column, where CO_2 chemisorbs into an amine solvent (MDEA), catalyzed by CA, and a proton and a bicarbonate ion is generated. The CO_2-depleted flue gas is released into the atmosphere and the bicarbonate-loaded amine solvent along with CA was transferred to a second column, where CO_2 was removed at elevated temperatures (>87 °C), resulting in solvent regeneration. The pure CO_2 stream can be compressed and stored in depositories or used in industrial processes. The regenerated solvent is returned to the absorber column to repeat the process. A highly thermostable variant of DvCA was used in this process (Fig. 3). Use of directed evolution technology led to the marked enhancement in the properties of a β-CA from *Desulfovibrio vulgaris*. Several rounds of library design, library generation, high throughput screening led to the selection of highly stable CA variant that even can retain its activity at 107 °C (Alvizo et al. 2014). This enzyme has more than 40% residual activity at 82 °C at highly alkaline pH (11.8) in the presence of 5 M MDEA.

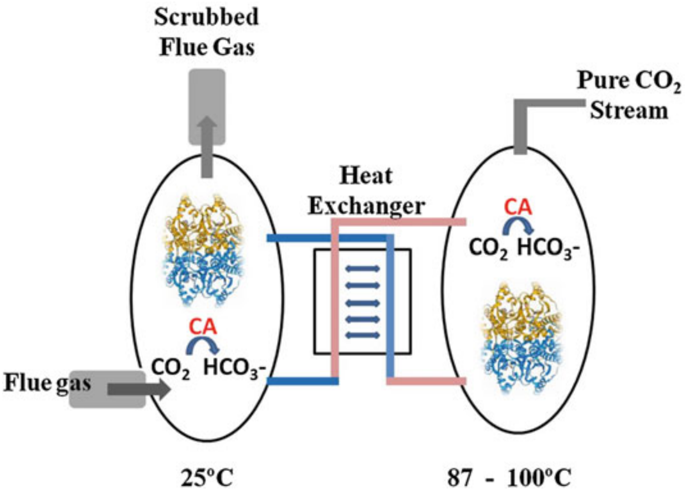


Fig. 3 Flue gas from a coal-fired power plant is piped into an absorber column (*blue*), where CO_2 chemisorbs into an amine solvent, catalyzed by CA, and is hydrated to a proton and a bicarbonate ion (adapted from Alvizo et al. 2014) (Color figure online)

Cordexis has also developed novel carbonic anhydrases via directed evolution technology that increases the rate of carbon capture 25-fold under industrial conditions. This strategy has helped in the development of highly efficient CA enzyme which is highly thermostable and alkalistable. About 10 million folds improvement in thermal stability was achieved. It also retains its activity in the presence of wide variety of flue gas contaminants such as NO*x*, SO*x*, and others. It was also found to be extremely stable when it was subjected to high (4.2 M) concentrations of N-methyl-diethanolamine (MDEA). The enzyme was stable at 4.2 M MDEA at 50 °C for about 14 weeks. The half-life ($T_{1/2}$) increased by five times to 20 h in 4.2 M MDEA at 75 °C (Newman et al. 2010). A company (Protelica) has initiated a project on carbon capture and storage which will utilize genetically (directed mutation) engineered CA. This project aims at the development of thermo-alkali-stable analogs of CA which can withstand harsh conditions that arise during CO_2 capture (http://www.protelica.com/ Carbonicanhydrase).

Recombinant DNA technologies have also been used to develop novel immobilization strategies to develop stable variants of carbonic anhydrases using γ-CA from *Methanosarcina thermophila* and *Pyrococcus horikoshii* (Salemme and Weber 2013). This technique describes the development of γ-CA nanoassemblies, where single enzyme entities are attached with each other resulting in numerous linked interactions with the reactor surface. Some of the specific enzyme residues were mutated to cysteines, to create sites for biotinylation, thereby ensuring the formation of definite nanostructures by cross-linking biotinylated-γ-CAs with streptavidin tetramers (Salemme and Weber 2013). Extra addition of an immobilization sequence at amino- or carboxy-terminus aids controlled and reversible immobilization of the γ-CA to a functionalized face. The use of immobilized thermostable CAs, thus, will be useful in CO_2 capture processes.

7 Other Biotechnological Application of Carbonic Anhydrases

Apart from role of CAs in mitigating global warming, they have many other physiological functions as already stated above. This class of enzymes can also be used for other medical and related applications.

7.1 Artificial Lungs

One of the most predominating health problems today is respiratory failure (Ware and Matthay 2000). Unfortunately, use of ventilators can create many problems for patients including decreased lung efficacy because of overpressurized or overdistended lung tissue (Maggiore et al. 2003). To solve this problem artificial lung can be employed. It is a device capable of assisting with respiration without input from the lungs. The main bottleneck of this technique is the inadequate transfer of CO_2 per square inch across the polymetric hollow fiber membranes (HFM) used in this technology. One of the proposed method is to increase the rate of CO_2 transfer is immobilizing CA onto the HFM. The enzyme is added to the surface of the HFM. Higher rate of CO_2 transfer (75%) was seen within the CA-treated membrane as compared to that of the without CA-treated HFM. These findings suggest the possibility for the use of CA in manufacture of smaller artificial lungs, which could function effectively within the human body (Kaar et al. 2007).

7.2 Biosensors

The high attraction of HCA II for zinc (4 pM) (Lindskog and Nyman 1964) has been widely exploited to measure trace amounts of zinc in sea and wastewater (Thompson and Jones 1993) to check its toxicity to certain plants, invertebrates, and fish (Rout and Das 2003; Muyssen et al. 2006). However, the slow removal rate of zinc from the CA active site ($t_{1/2} \approx 90$ days [Lindskog and Nyman 1964]) limits the reusability and efficiency of the system. An HCA II variant (E117Q) that contained both a lowered binding affinity to zinc (nM) and had a much faster dissociation time ($t_{1/2} \approx 3$ s) for zinc was developed to circumvent these limitations (Huang et al. 1996). Efforts are underway to develop variants with a lowered binding affinity for other transition metals. Also biologically prevalent divalent metals such as Mg^{2+} and Ca^{2+} do not bind to CA and hinder the assay, biosensors employed in biomedical applications are especially useful (Frederickson et al. 2006; Thompson et al. 2000, 2002; Bozym et al. 2008; Wang et al. 2011; McCranor et al. 2012).

7.3 Pharmalogical Considerations

Stimuli-triggered drug delivery could be incorporated with CAs utilizing CO_2, bicarbonate, or pH changes as signaling molecules (Satav et al. 2010). This treatment involves a feedback-regulated antidote delivery system that responds to high CO_2 levels or decrease in pH (Satav et al. 2010). The cationic hydrogel is made from *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) polymers having a pKa ~ 7.5, which makes it an adequate blood pH monitor. Incorporation of CA as a CO_2 sensor improves the efficiency of these antidote delivery systems (Satav et al. 2010).

7.4 Blood Substitutes

The major drawback of current blood substitutes, is the inadequate CO_2 removal rate which can lead to coma and ultimately death. CAs along with catalase (CAT), superoxide dismutase (SOD) can be encorporated to the PolySFHb substitute (PolySFHb-SOD-CAT-CA) to overcome this limitation with encouraging activity (Bian et al. 2012).

8 Future Perspectives

Genome sequencing and metagenomics have led to the discovery of many new organisms with distinctive features. Daily many more are discovered and their genomes are sequenced. Sequencing and annotations have helped us to identify and exploit special features of these organisms for human needs. Many CA genes have been identified in a number polyextremophilic life forms (Ferry 2010) with the help of metagenomic and genome mining studies. About 75 β-carbonic anhydrase sequences have ben found in metazoan and protozoan species by proteome-wide searches and multiple sequence alignment (Emameh et al. 2014). Metagenomic studies showed the presence of gene-encoding CA in the viral metagenome of Indian Ocean (Willamson et al. 2012). The community genome analysis revealed the presence of CA and RuBisCo gene clusters in the *Acidithiobacillus* of an extremely acidophilic sulfur-oxidizing biofilm (Jones et al. 2012). At least three copies of genes that code for carbonic anhydrases have been reported in the metagenome of the marine ammonium oxidizing bacterium (Van deVossenberg et al. 2013). CAs have their signatures in all the three domains. These analyses have demonstrated that carbonic anhydrases are ubiquitous among metabolically and phylogenetically diverse prokaryotes from both the bacteria as well as archaea. The current available metagenomic data reveals the presence of many putative carbonic anhydrase-encoding genes from extremophilic sources. These are mostly unculturable. Bioinformatic techniques like translated genome inspection and data mining are very useful in identifying these genes. These genes can be cloned and expressed in *E. coli* to study their novel properties and usefulness in various biotechnological applications. There are very few reports available on cloning and characterisation of novel CAs from polyextremophilic sources and characteristics of these CAs are still unknown. Exploring them might reveal an array of new features concerning the enzyme, which will add up to their existing potential. Development of highly efficient and robust CAs from polyextremophilic microbial sources followed by genetic engineering will lead to cost-effective biomimetic carbon capture technologies.

9 Conclusions

Global warming is the main culprit for climate change, majorly caused due to increased CO_2 emission. Most of the countries in the world are in developing stage and it is tough for them to cut down their carbon emissions as they are mostly dependent on fossil fuels. There has to be a way to control increasing carbon emissions and it is indispensable to develop strategies for mitigating CO_2 in the atmosphere. Biological methods such as afforestation, algal cultivation, and biomineralization are some of the potential approaches. In this context, the utility of carbonic anhydrases, ubiquitous Zn^{2+}-metalloenzymes, in converting carbon dioxide into bicarbonate is very important. CAs from mesophilic sources would not be stable at higher temperatures as well as alkaline pH. These two features are essential for mineralizing flue gas CO_2. CAs from polyextremophilic sources, therefore, can be promising candidates. The polyextremophiles are often very difficult to cultivate and to produce enzymes in adequate quantities. Recombinant DNA technology has been widely used to overcome the bottlenecks. Cloning and heterologous expression of CAs from polyextremophilic bacteria have already been achieved. Many CA-encoding genes are being discovered from various metagenomes. Currently six classes of carbonic anhydrases with distinct properties have been discovered. Further research efforts are called for developing CAs with desirable properties and immobilization strategies for application in carbon sequestration.

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Part III

Low Carbon Growth Strategy from CO_2 Utilization

Chapter 9
Climate Change Mitigation via Utilization of Carbon Dioxide

K. Palanivelu

Abstract Carbon dioxide is a waste product in many industries, especially from thermal power plants and is a major contributor to global warming. The large scale solution to the problem of CO_2 emissions currently being considered is carbon capture and storage (CCS). In CCS, the CO_2 is first separated from the flue gas by capture techniques and then later stored underground. This method does not eliminate CO_2; it just stores it. Environmental threats of escape are spurring re-evaluation of CCS to eliminate CO_2 rather than move and store it. A more attractive solution would be carbon capture and utilization (CCU) in which the waste CO_2 is not dumped, but converted into a commercially valuable product. The growing re-evaluation of carbon capture strategies emphasizes transforming CO_2 to valuable chemical rather than storing it. This chapter gives an overview to cover the work carried out on CO_2 from flue gas, and how it could be converted into a valuable chemical for which there is a demand. This article first covers briefly the CO_2 separation or capture from flue gas and storage and then the technologies to convert the separated CO_2 into usable chemicals employing methods, such as chemical, photochemical, electro-chemical and bio-process. The proper use of CO_2 from waste flue gas is expected to provide both environmental and economic benefits.

Keywords Carbon dioxide · Climate change mitigation · Capture · Utilization Value added products

Abbreviations

Mt	Million tons
FTMs	Facilitated transport membranes
RM	Red mud
CFA	Coal fly ash

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SS	Steelmaking slag
AMP	Amino methyl propanol
DES	Deep eutectic solvent
cPANFs	Carboxylated polyaniline nanofibers
Mag-EPC	Magnetically separable enzyme precipitate coatings
PVA	Polyvinyl alcohol

1 Introduction

Over the past decades, rapid global energy demand has been driven by a growing world population. Present energy infrastructure is almost dependent upon fossil fuels. Fossil fuels combustion produces greenhouse gas CO_2 which traps heat and raises the global temperature, contributing to climate change. There are various sources of CO_2 emissions, which are dominated by combustion of liquid, solid and gaseous fuels. As of December 2015, CO_2 is present in the atmosphere with a volumetric concentration of 0.040%, (NOAA 2016). The global warming issue is one of the important development-based environmental issues that impact the very foundations of human survival and ecosystem. To avoid dangerous climate change, the increase in atmospheric concentration of the main agent, CO_2 must be reduced. In order to cope with global warming problem, a variety of measures have been proposed and/ or implemented worldwide for mitigating the warming. The options to reduce CO_2 emission into the atmosphere are the following:

- Reduce energy intensity which requires efficient use of energy
- Reduce carbon intensity which requires switching to using non-fossil fuels such as hydrogen and renewable energy, and
- Enhance the sequestration of CO_2 with the development of technologies to capture, sequester and utilize more CO_2.

The recent “Paris Agreement” of the twenty-first Conference of the Parties (COP) a legally binding treaty on climate actions which contains emission reduction commitments from 187 countries during 2021–2030, to avoid the rise in temperature by 2.0 °C in 2050, with all efforts to be made to contain it to 1.5 °C.

2 Main Sources of CO_2

The world’s commercial energy needs are currently derived from fossil fuels-based thermal plants. A rapid change to non-fossil energy sources would result in large disruption to the energy supply infrastructure, with substantial consequences for the global economy. The CCS technology would enable the world to continue to use fossil fuels but with much reduced emissions of CO_2, while other low-CO_2 energy

Table 1 Worldwide large CO_2 emitting source

S.no.	Process	Emission (Mt of CO_2/year)
1.	Fossil fuel power	10,539
2.	Cement production	932
3.	Refineries	798
4.	Iron and steel industry	646
5.	Petrochemical industry	379
6.	Oil and gas processing	50
7.	Other sources	33
8.	Biomass (Bioethanol and bioenergy)	303

Source Lotz and Brent (2008)

sources like solar and wind become cost-effective and introduced on a reasonable scale. Global emissions of CO_2 from fossil fuel use were 23,684 million tonnes (Mt) in 2001. These emissions are concentrated in four main sectors: power generation, industrial processes like cement, iron and steel and oil refining, the transportation sector and residential and commercial buildings and are normally in the range 4–14% of CO_2 by volume. The worldwide large CO_2 emitting sources are furnished in Table 1. The anthropogenic emission (32,000 Mt/y) value (Aresta 2013) has currently exceeded. The future global emissions would range from 270 to 1685 Gt-C in 2100 depending on the implementation of mitigation measures adopted globally.

3 CO_2 Capture

CO_2 capture is a key climate change mitigation technology for mitigating the unfettered release of CO_2 into the atmosphere and is currently in the process of being demonstrated worldwide. To keep this gas at manageable levels, large reduction in CO_2 emissions through capturing and separation is needed. Currently, a variety of technologies are being evaluated for their ability to capture CO_2 from power and other stationary industrial plants flue gases.

Various Carbon capture and Storage (CCS) technologies offer great potential for reducing CO_2 emissions and mitigating global climate change. The idea of CO_2 capture is to produce a stream of pure CO_2 gas from a mixture of CO_2 and other gas components. There are many ways to perform this operation, such as Absorption, Adsorption, Membranes, Distillation, Mineralization and Thermal processes. None of the capture options are a clear winner at this point.

The most commercial ready technology amine absorption is costly, energy intensive, and if implemented, would result in large increases in the cost of producing electricity. Membrane-based gas separation is today well consolidated and considered alternative for cryogenic distillation, absorption and pressure swing adsorption. Membranes compete with other separation processes on the basis of overall economics, safety and environmental and technical aspects.

Polymeric membranes are generally being used in industries for CO_2 gas separation. However, the major problem associated with the polymeric membrane-based CO_2 separation is the lack of membranes with high permeability and high selectivity. This could be overcome by facilitated transport membranes (FTMs). FTMs are the membranes, in which the CO_2 selective carrier is incorporated into the polymeric membrane, which facilitates the spontaneous passive transport (as opposed to active transport) of molecules across a membrane. The carrier contains a special affinity towards the target gas molecules and this interaction controls the rate of transport (Marzouqi et al. 2005).

4 CO_2 Storage

The captured CO_2 can be transported and disposed in natural sites such as deep geological sequestration mineral carbonation, or ocean storage. There are three geological formations that have also been recognized as major potential CO_2 sinks: deep saline-filled sedimentary, depleted oil and natural gas reservoirs and unmineable coal-seams. The geology also suggests possibilities for CO_2 enhanced oil recovery, CO_2 enhanced gas recovery and CO_2-enhanced coal-bed methane recovery, such projects will be most beneficial in nature. However, just storage underground may not be a good option for the long-term risk associated is not known. Submarine storage would increase the possibility of ocean acidification affecting the marine ecosystem.

Waste CO_2 from onsite flue gas is combined with limestone and stored within precast concrete products. Concrete curing with CO_2 limits the need for heat and steam during the curing process. This technology is still in development and its competitiveness with traditional methods of curing concrete will depend on whether or not it will reduce costs. CO_2 can be carbonated in alkaline wastes safely and could be used as building material or stored. In the process, direct mineral carbonation of red mud (RM), coal fly ash (CFA) and steelmaking slag (SS) were carried out in mild conditions with 100% pure CO_2 gas and at high process conditions with flue gas containing 15% CO_2. In the case of carbonation studies with flue gas, maximum sequestration capacity of 15.5 g of CO_2/kg of RM (65.1 °C,

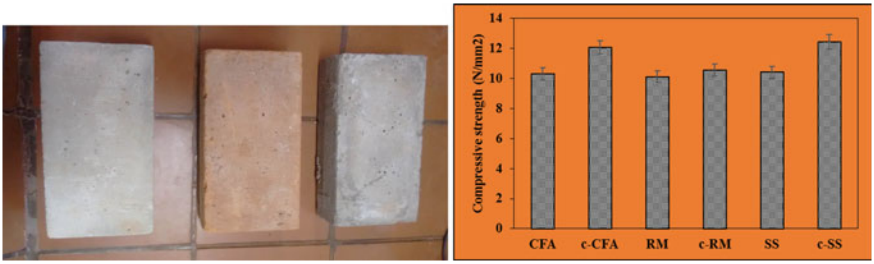

Fig. 1 Photographs showing the carbonated alkaline waste bricks and their strength comparison with pain one

42.11 bar, L/S ratio-0.53, and 40 min), 51.0 g of CO_2/kg of CFA (61.6 °C, 48.7 bar, L/S ratio-13.35, and 50 min) and 127.4 g of CO_2/kg of SS (61.1 °C, 46.24 bar, L/S ratio-14.5, and 40 min) was attained. Carbonated wastes were further used for making masonry bricks and the tests on compressive strength and water absorption capacity indicated the good quality of them as shown in Fig. 1. These findings demonstrated that industrial solid wastes which are available in huge quantities in the world, pose to be a promising resource for carbon capture and storage and development of a potential technology towards mitigation of CO_2 emissions. Moreover, the carbonated wastes could be used for making eco-friendly products in the construction sector (Revathy et al. 2015; Pan et al. 2012).

5 CO_2 Utilization

There are essentially two pathways for utilizing CO_2: non-conversion use of CO_2 and utilization of CO_2 as a feedstock for chemicals. Both the utilization technologies together have the potential to reduce CO_2 emissions by at least 3.7 Gt/y (approximately 10% of total current annual CO_2 emissions), both directly and by reducing use of fossil fuels. However, much greater reductions are possible through wider adoption of these technologies.

5.1 *Non-Conversion Use of CO_2*

CO_2 can be used in its supercritical state as the solvent for de-caffeinating coffee. In desalination process, CO_2 mixed with H_2O brine at high pressure and low temperature, forms a hydrate of CO_2 surrounded by H_2O molecules. The hydrate is removed and rinsed, then goes through multiple stages to remove dissolved solids in the brine, resulting in an exhaust stream of potable water. CO_2 can be applied to a fire to reduce the oxygen level low enough to stop combustion. It is also used in fire extinguishers and fire protection systems. CO_2 can be used during food processing for things such as cooling or spoilage prevention, and also during packaging as an inert atmosphere to extend the shelf life of food products. Supercritical CO_2 could be used either as the circulating heat exchange fluid or as the working fluid in a supercritical CO_2 geothermal power cycle (Huang and Tan 2014).

5.2 *Chemical Synthesis*

Turning CO_2 into a useful feedstock chemical could help to reduce levels of this greenhouse gas in the atmosphere, as well as providing a cheap source of carbon. This section covers the various CO_2 utilization technologies reported so far. They are non-catalytic chemical processes, photo-catalytic reduction, bio-chemical and enzymatic conversion, electrochemical reduction as well as solar-thermal/catalytic processes.

The synthesis of urea from ammonia and the production of salicylic acid from phenol and CO_2 are representative examples of chemical process used in industries. Soda lime (mixture of sodium and calcium hydroxides) are well known for their assistance in the stoichiometric transformation of CO_2 to carbonate salts. Mixtures of glycol and amines (glycol-amine) as well as coordination complexes of polyamines have been reported to bind CO_2 reversibly through the formation of carbamates. Insertion of CO_2 into epoxides to manufacture various polymeric materials is an exciting technology as it not only utilizes CO_2, but also avoids using fossil feedstock and creating CO_2 emissions.

Modified Solvay process is a novel approach that utilizes a chemical reaction for converting the industrial waste gas—CO_2 to a valuable bicarbonate product using textile, effluent. In the process, CO_2 is passed into an ammoniated brine solution, which reacts with sodium chloride and/or sodium sulphate to form a precipitate of sodium bicarbonate and a soluble ammonium chloride according to the following equation:

$$NaCl + NH_4OH + CO_2 \rightarrow NaHCO_3 \downarrow + NH_4Cl \qquad (1)$$

The briny textile dye bath effluent was successfully used as a raw material for the valuable bicarbonate chemical production using the captured CO_2. From the experimental results, it can be concluded that the highest Na^+ removal of 38% could be obtained and the optimized reaction conditions were as follows: NH_4OH/Na^+ ratio of 2, reaction temperature of 20 °C, flow rate of the CO_2 of 1.8 L/min and carbonation time of 150 min. The results indicate that the new approach can be designed to reduce CO_2 gas emissions, as well as to decrease the Na^+ in textile effluent by recovering it as sodium bicarbonate (Krishnaveni and Palanivelu 2013). This could also be used for RO reject of tannery effluent and desalination plant.

The efficient conversion of captured CO_2 into useful compounds is a long standing dream of synthetic chemists. Catalysts play a key role in expanding the synthetic potential. Efficient catalytic conversion of captured CO_2 to chemicals could be a major contributor towards achieving carbon neutrality. Inorganic and organic carbonates, carbamates and acids are the main products during the chemical conversion of separated CO_2. Reactions of alcohols and amines with CO_2 are good avenues for the production of carbonates and carbamates. Cyclic carbonates have been widely used as raw materials for polycarbonates, electrolytes in lithium-ion secondary batteries, aprotic polar solvents and fuel additives (Dai et al. 2009).

$$2ROH + CO_2 \rightarrow ROCOOR + H_2O \qquad (2)$$

$$2RR'NH + CO_2 \rightarrow RR'NH_2OOCNRR' \qquad (3)$$

Ultrasound has been proven to be a potentially useful tool for intensification of carbonation processes. The synthesis of β-resorcylic acid based on Kolbe–Schmitt reaction from CO_2 under ultrasonic and mild conditions was evaluated. The influences of carbonation time, flow rate of CO_2 and the molar ratio of resorcinol/potassium hydroxide on the yield percentage of resorcylic acid were investigated. The amount of CO_2 utilized in the reaction was evaluated from the yield of resorcylic acid. The maximum yield of resorcylic acid of 30 and 65% were obtained at the resorcinol/potassium hydroxide ratio of 1:3, carbonation time of 150 min and the CO_2 flow rate of 2 L/min in bath and horn type ultrasonication, respectively (Shanthi and Palanivelu 2015).

Conversion of CO_2 into carbamates is another interesting approach. Carbamates are important raw materials for the manufacture of a variety of polymers used in foams, coatings, adhesives, plastics and fibres. It is being used as an insecticide, human medicine and as a preservative. Current commercial processes for production of carbamates are alcoholysis of isocyanates or aminolysis of chloroformates. The preparation of isocyanates and chloroformates requires use of the highly toxic and corrosive phosgene ($COCl_2$). Alternative routes imply the utilization of poisonous carbon monoxide, or rather expensive dialkyl carbonates (Carloni et al. 2002). Use of CO_2 in carbamate synthesis is particularly attractive, since CO_2 is a non-toxic, non-corrosive, inflammable, abundant and cheap C1 source. In this context, non-aqueous 2-amino-2-methyl-1-proponal (AMP) was used for the conversion of CO_2 into the value-added product, carbamate. The non-aqueous media employed are vegetable oil and deep eutectic solvent (DES). AMP-carbamate of 56% (3 M, 35 °C, 90 min, and 10 bar) and 82% (3 M, 35 °C, 60 min, and 6 bar) was obtained from coconut oil and ChCl: U (1:2) medium. By this novel approach, CO_2 gas was captured as well as utilized with the recovery of value-added products (Maheswari and Palanivelu 2014, 2015).

5.3 Photo-Chemical Reduction

Photo-chemical CO_2 reduction harnesses solar energy to convert CO_2 into higher energy products. Because of the stability of CO_2, energy is needed to drive the desired transformations; moreover, its inertness necessitates the use of catalysts. Transition-metal complexes are used as catalysts since they can absorb a significant part of the solar spectrum, have long-lived excited states and can promote the activation of small molecules. Photo reduction of CO_2 on irradiated semi-conductor surfaces has been widely reported to give a range of C1 and C2 products, including CO, formate, methanol, methane, formaldehyde, oxalic acid and glyoxal. CO_2 photo reductions are observed on a variety of metal oxides, including WO_3, TiO_2, ZnO, as well as on GaP, ZnS and CdS. Reductions are believed to result from photo promotion of hole/electron pairs in the oxide/sufide conduction bands, capture of electrons by CO_2 and whole oxidation of water or some added reducing agent. Photo efficiencies for CO_2 reduction appear to range from less than 1–23% on certain quantized oxide particles (Yoneyama 1997, Inoue et al. 1990). The high efficiencies also appear to require large band gaps, thus reducing efficient use of the full spectrum of sunlight (Boston et al. 2013; Wang et al. 2015).

5.4 Electro-Chemical Reduction

Electrochemical activation of CO_2 using metallic modified cathodes and metal-free electrodes (Xianwen and Hatton 2015), has long been studied, and significant progress has been made. Various reduction products can be formed via different reaction pathways; the main products include formic acid, oxalic acid, formaldehyde (CH_2O), methane (CH_4) and many others. Using metal or metal-free electrodes/catalysts, various products can be produced by electrochemical reduction of CO_2, including formic acid (HCOOH), oxalates ($C_2O_4^-$), hydrocarbons and alcohols (e.g. methanol, CH_3OH). Though the electrochemical reduction method has several advantages, such as conversion at room temperature and ambient pressure, use of renewable energy to run the system, compact design, etc. still vast improvement in conversion yield is required (Gattrell et al. 2006). A preliminary attempt by our group using a solar powered divided cell as shown in Fig. 2 in CO_2 reduction with stainless steel cathode gave encouraging yield of formic acid.

5.5 Bio-chemical Methods

The enhancement of the growth of plants as a result of increased atmospheric CO_2 concentration. Depending on their mechanism of photosynthesis, certain types of plants are more sensitive to changes in atmospheric CO_2 concentration. In particular, plants that produce a three-carbon compound (C3) during photosynthesis including most trees and agricultural crops such as rice, wheat, soybeans, potatoes and vegetables generally show a larger response than plants that produce a four-carbon compound (C4) during photosynthesis mainly of tropical origin, including grasses and the agriculturally important crops maize, sugar cane, millet and sorghum. Utilization of CO_2 as an industrial by-product for seaweed production holds great promise not only in acting as a significant sink, but also in meeting to

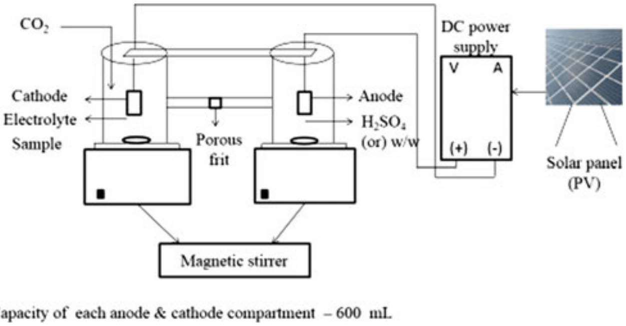

Fig. 2 Experimental Setup

some extent global food, fodder, fuel and pharmaceutical requirements, particularly in the tropics (Aresta et al. 2005).

Biological products derived from them, such as agars, alginates, have and will continue to have diverse applications in the food, chemical, pharmaceutical and other industries. It is interesting to note that 3.5 t of algae production utilizes 1.27 t of carbon and about 0.22 t of nitrogen and 0.03 t of phosphorus. The utilization of seaweed colloids in the industry remains to be one of the more exciting aspects of the world seaweed production. Prospects for the seaweed culture industry appears very promising in the Asian region with the growing demand for seaweeds primarily as food resources with increasing population in the tropics and also for raw materials for industrially useful seaweed extracts.

5.6 CO_2 Utilization via Microalgae

CO can be combined with (bubbled through) algae cultivation systems to increase algae yield. The increased algae product can be a feedstock for biodiesel, food products and chemicals; it can also be reformed into a variety of other products. Moreover, CO_2 can indirectly be applied in the cultivation of microalgae as well, making microalgae a potential alternative to solve energy and environmental issues. Therefore, replacing about 5% of liquid fuels with biofuel, and assuming a 50% life cycle reduction in CO_2 emissions in comparison with petroleum-based fuel, has the potential to reduce CO_2 emissions by 0.4 Gt/y (Aresta et al. 2005).

5.7 Enzymatic Conversion of CO_2

Among the current major methods (including chemical, photochemical, electrochemical and enzymatic methods), the enzymatic method, which is inspired by the CO_2 metabolic process in cells, offers a green and potent alternative for efficient CO_2 conversion due to its superior stereo-specificity and region/chemo-selectivity (Shi et al. 2015). The process based on one-pot CO_2 conversion and utilization based on simple conversion of CO_2 to bicarbonate at ambient temperature with no energy input, by using the cross-linking-based composites of carboxylated polyaniline nanofibers (cPANFs) and carbonic anhydrase was reported. Carbonic anhydrase was immobilized on cPANFs via the approach of magnetically separable enzyme precipitate coatings (Mag-EPC), which consists of covalent enzyme attachment, enzyme precipitation and cross-linking with amine-functionalized magnetic nanoparticles. This one-pot CO_2 conversion and utilization is an alternative as well as complementary process to adsorption-based CO_2 capture and storage as an environmental friendly approach, demanding no energy input based on the effective action of the stabilized enzyme system (Shi et al. 2015).

Opportunities and challenges in carbon dioxide capture and CO_2 recycling/utilization in the perspective of industrial ecology also have been recently reviewed (Meylan et al. 2015).

6 Conclusion and Way Forward

The accumulation of CO_2 in atmosphere has caused the global climate change. Carbon-based fossil fuels will continue to be the main energy source in the short and medium term but it is necessary to control the CO_2 emission to the atmosphere. The combination of CO_2 capture and conversion to useful product is an attractive approach to solve the global warming effect partially.

Besides storage underground to get enhanced oil and gas, CO_2 can be used directly in different industrial sectors, including the food and beverage as well as supercritical solvent industries and in cleaning. It can also be converted into high-demand products such as urea, methanol and biofuels.

The separation of CO_2 from the mixture of CO_2 and N_2 gases using PVA-amine blend membranes was successfully analyzed. The best CO_2 selectivity of 50 over N_2 was attained in the separation process. Converting the captured CO_2 to valuable carbamate, carbonate, carboxylic acid and other chemicals is one of the best ways of preventing a rise in temperature due to the greenhouse effect.

Further research and development of membranes will probably improve their performance (better selectivity and reduced cost). It is believed that membranes can be a very interesting alternative in the future.

Utilization technologies especially for stationary industrial sources hold promise by helping to mitigate significantly its environmental impact with simultaneous generation of saleable chemical products in a sustainable way from this waste CO_2 gas. Various chemicals, materials and fuels can be synthesized using CO_2, which should be a sustainable way in the long term when renewable sources of energy such as solar energy is used as photon in Photo/Electrochemical process and energy input for the chemical processing. CO_2 utilization will be an economical method especially for industries, such as refineries, which cannot implement CCS economically.

The future trends for controlling CO_2 emission and accumulation in the atmosphere with appropriate new technology should focus on the following:

- Reducing fossil fuel use or switching to less CO_2 intense fuels such as carbon neutral biofuels and H_2.
- Using more efficient energy systems for energy conservation.
- Increasing the contribution of alternative energies such as solar, wind, geothermal-energy, etc.
- Developing and improving the capture and separation technologies that are economically sound and effective.
- Developing and improving environmentally benign CO_2 storage, including terrestrial biomass and alkaline wastes.
- Utilizing the separated CO_2 by emphasis on fostering and chemical processes with renewable energy and catalysts and integrated technologies.
- Developing synthetic systems that may mimic nature for enhanced CO_2 sequestration.

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Chapter 10
Carbon Sequestration Through Solar Bioreactors: Industrial Strategies

K. Sudhakar and Ruma Arora Soni

Abstract A promising biological solution for the utilization and conversion of CO_2 from a power plant into viable economic products has been discussed in this study. Algae grow well on a high concentration of carbon dioxide and nitrogen dioxide. These pollutants which are released by automobiles, cement plants, breweries, fertilizer plants, steel plant scan serve as nutrients for the algae growth. The biotechnology of microalgae production can be divided into the following different types as cultivation systems, ponds and Photobioreactorsas closed system with associated harvesting and processing equipment and the wetware as the specific algae species and strains are being cultivated. Algae when used for reducing the carbon dioxide concentration in the atmosphere are known as algae-based Capture technology. The algae-growing facilities when fed with the exhaust gases from these plants to significantly increase the algal productivity and reduce the pollutants from atmosphere. Additionally the oil found in algae can be processed into a biodiesel or green fuel. Additional products from algae includes ethanol and livestock feed. This technology offers a safe and sustainable solution to the problems associated with global warming. The value-added products that can be produced from these four main technologies are biomass with both low and high grade, biomass derived products as pharmaceutical, chemical or nutritional, synthesis gas as methanol, fuel and chemical production, speciality products as extracted using supercritical technology, organic carbonates as linear, cyclic or poly-carbonates, carboxylates as formic acid, oxalic acid, etc. along with salicylic acid and urea.

Keywords Algae based capture · Biomass · CO_2 Mitigation · Industries · Biodiesel

Abbreviations

SO_x	Sulphur oxides
NO_x	Nitrogen oxides

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1 Introduction: Carbon Capture and Storage

Since many years, several different approaches to capture and store carbon dioxide have been emerged and studied as potential climate change mitigation options (Campbell et al. 2009; Sudhakar et al. 2012a, b). The most prominent and efficient approaches can be grouped among following three categories:

- Biological storage or Biological Carbon sequestration
- Ocean storage
- Geologic storage

Photosynthetic processes can convert CO_2 into biomass, which further can be used or in turn converted to biomass fuels that can replace fossil fuels, for electricity production or in different economical sectors as transportation (Benemann et al. 1980). Plant photosynthesis is reported as a major world-wide source of fuels, with biomass fuels representing about 15% of all primary energy consumption (Scurlok and Hall 1990). Biomass fuels could displace a major fraction of current fossil fuel consumption, particularly if CO_2 mitigation were to become a policy and economic goal. Biomass production takes place in the presence of atmospheric levels of CO_2; the concentrated CO_2 present in flue gases is not required. Nevertheless, it is well known that plants exhibit higher productivities under elevated levels of CO_2. In greenhouses, elevated levels of CO_2 are routinely used to increase plant production. The cultivation of algae, both the seaweeds and the smaller microalgae, requires an enriched source of CO_2, as the transport of CO_2 from the atmosphere into the growth ponds is not sufficient to support their growth.

Biological carbon storage has received more attention as it involves enhancing the natural photosynthetic process where atmospheric carbon dioxide is used up by green plants and then converted to organic carbon. The other major benefits which are associated with efforts to enhance biological carbon storage and the minimal negative environmental impacts; biological carbon storage has been most commonly used, supported and widely accepted within the environmental community (Sudhakar et al. 2012a, b; Becker 1994).

The second approach to carbon storage involves storing CO_2 captured from power plants in oceans. Theoretically this approach is appealing as the oceans have the capacity to store most of the CO_2 that is currently being emitted into the atmosphere, whereas concerns about the ecological impacts of increasing the oceans uptake of carbon dioxide by injecting it into the oceans have limited research and advancement of this approach (Becker 1994).

The third approach Geological storage of carbon, involving the injection of captured CO_2 into underground geological reservoirs is the approach that has emerged in the past 5 years with the greatest potential to stabilize atmospheric CO_2 emissions. The CO_2 gas is captured and subsequently stored in an underground geological reservoir.

Among above approaches, biological carbon storage although being the easiest has the least involvement of technology. The idea of planting trees as a way to mitigate climate change has been previously proposed, and this idea resonates with those concerned about the environment in part due to other associated environmental benefits of facilitating forest growth (Sudhakar et al. 2011, 2012a, b).

2 Capturing and Recycling of CO_2

For microalgae, water, nutrients and carbon dioxide are vital to growth. The growth of microalgae is limited due to atmospheric CO_2. So a supplement is required and industrial and power plants fired with fossil fuels could be such a source adding extra revenues from greenhouse gases abatement to microalgae production (Becker 1994; Sudhakar and Premalatha 2012a, b, c). The general concept of CO_2 Capture through microalgae ponds/bioreactors are shown in Figs. 1 and 2.

The main purpose of algae cultivation is to sequester the industrial CO_2 outputs of fossil fuelled power plants, and therefore it has to be taken into account, as during the night the growth of algae slows down as their reproduction rate is also decreased and thus it utilizes less CO_2. Gas storage facilities should be installed to cope with the influx of CO_2 during night.

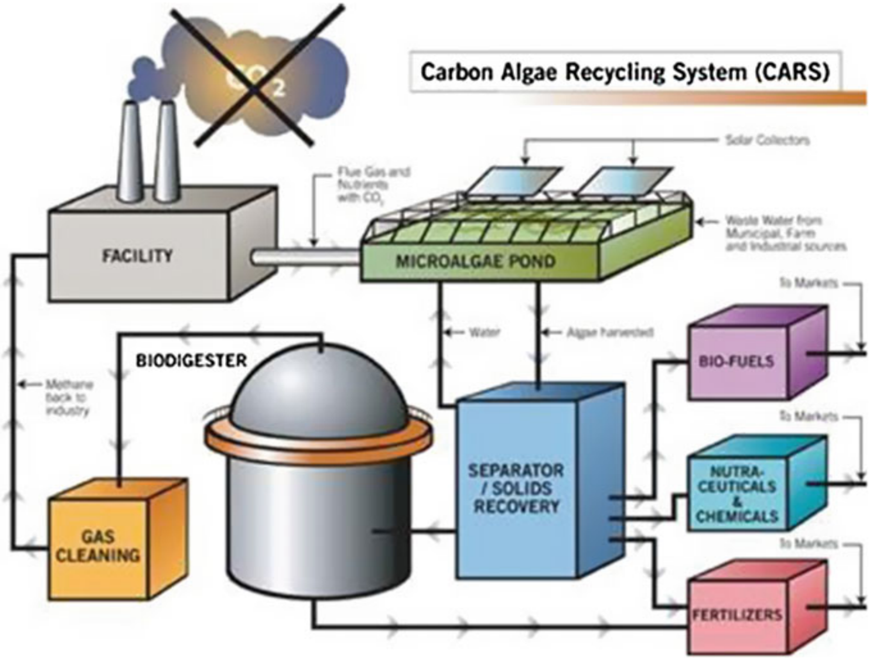

Fig. 1 Carbon algae recycling system, Christine et al. (2009)

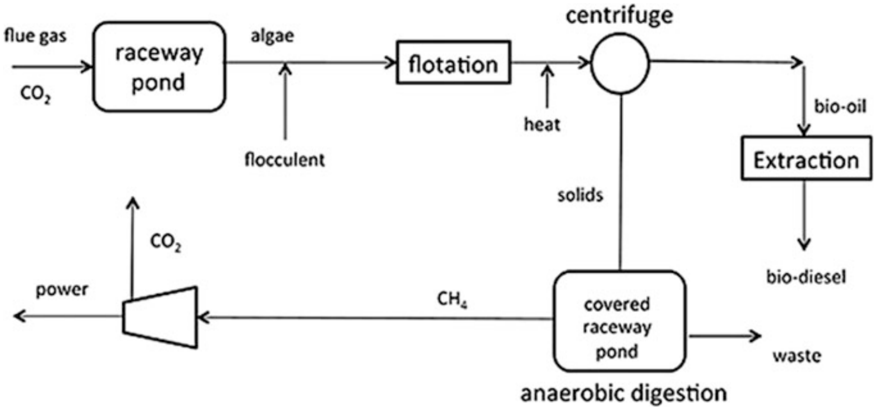

Fig. 2 Schematic diagram of algae process from Campbell et al. (2009)

The amounts of carbon dioxide consumed for making the chemical products are relatively small, but the benefits of the value-added products and the environment friendly processing plus the carbon dioxide avoidance compared to the conventional energy intensive or hazardous processes make carbon dioxide utilization an important option in carbon dioxide management (Borowitzka 1999). CO_2 must be captured, purified and concentrated prior to employment in most utilization methods. The feasibility of these processes was evaluated according to their thermodynamics, energetic, production rates and yields, product values and economics (Sudhakar and Premalatha 2012a, b, c).

3 CO_2 Mitigation Strategies for Industries

Carbon sequestration may be defined as the capture and secure storage of carbon that would otherwise be emitted to, or remain in the atmosphere (Herzog and Golomb 2004). CO_2 emission into the atmosphere can be reduced by following three ways (Yang et al. 2008):

(i) By reducing energy intensity use,
(ii) By reducing carbon intensity use, and
(iii) By enhancing the sequestration of carbon dioxide.

The first way requires efficient use of energy and the second one refers to the use of non-fossil fuels and the third option involves technologies to capture and reuse the CO_2.

Industrial exhaust gases contain about 10–20% CO_2 with small amounts of SOx and NOx. Some strains are inhibited by CO_2 when NOx is present whereas cannot be inhibited with <50 ppm SOx (Lee et al. 2002; Negoro et al. 1991). By chemical desulfurization method SOx can be easily eliminated from the flue gas whereas

Table 1 Comparison of the growth characteristics and CO_2 fixation performance of microalgae strains under different CO_2 concentrations, temperature and NOx/SOx contents

Microalgae species	CO_2 (%)	Temperature (0 °C)	NOx/SOx (mg/L)	Biomass productivity (mg/L/d)	CO_2 consumption rate (mg/L/d)
Nannochloris species	15	25	0/50	350	658
Nannochloropsis species	15	25	0/50	300	564
Chlorella species	50	35	60/20	950	1790
Chlorella species	20	40	Not specified	700	1316
Chlorella species	50	25	Not specified	386	725
Chlorella species	15	25	0/60	1000	1880
Chlorella species	50	25	Not specified	500	940
Chlorogloeopsis	5	50	Not specified	40	20.45
Chlorococcum littorale	50	22	Not specified	44	82

removal of NOx is bit difficult as it is less soluble in the liquid phase. Table 1 shows some microalgae species that are tolerant to high-temperatures, high CO_2 concentrations and toxity with NOx and SOx compounds. The selection of suitable microalgae strains for CO_2 mitigation has significant effect on efficacy and cost-competitiveness of the bio-mitigation process.

Major factor for industries are CO_2 aeration rate and light intensity. Enhancement of light utilization efficiency is substantial to obtain higher CO_2 fixation ability by the following:

- increasing surface area
- shortening the light path and layer thickness
- using genetic engineering
- Improvement of CO_2 transport efficiency
- Getting the extensive air/liquid interface area
- Increase mixing time/intensity
- Maintain CO_2/O_2 balance
- Increasing turbulence
- Stripping the culture medium with air or inert gas

CO_2 fixation rate of microalgae is lower than the available physicochemical methods (Sudhakar and Premalatha 2012a, b, c, 2015).

4 Biological CO_2 Utilization

Using biological systems to trap CO_2 from the power plant burning fossil fuel seems the most attractive with regard to potentially positive ecological results. There are certain water submerged microalgal species with a very high growth rate to be used by industries, for trapping and also for the utilization of CO_2 through conversion microalgae biomass into fuel.

With the increasing atmospheric carbon dioxide levels, global warming has become a major focus of the environmental agenda. The United States CO_2 production is on a rise from the already approximately 5.56 billion tonnes per year from coal-burning power plants (Apel et al. 1994). This ratio of CO_2 is equivalent to about 21% of the entire world's CO_2 production. The flue gases composition from power plants may vary slightly with the specific fuel type and the amount of air used in combustion. The flue gas compositions with different fuel sources consists of approximately 10% CO_2 (Mustacchi et al. 1978). Flue gas concentrations of up to 20% have been measured when coal is burned (Sakai et al. 1994). The biotechnology of using microalgae in a photobioreactor has extensively been studied since long back for reducing the quantity of CO_2 in atmosphere. With the biological approach, CO_2 is converted into algal biomass and then into value-added products such as proteins, vitamins, food and feeds. The concept of using outdoor macroalgal cultures in ponds, lakes, oceans or land has been proposed as a method to reduce CO_2 emissions (Guterman and Yaakov 1990). However, it is difficult to optimize algal growth in an open pond, resulting in low productivity of the process. The outdoor systems mainly struggle with low productivity, whereas closed photobioreactors may result in higher productivity without causing any more environmental issues (Laws et al. 1988). The use of photobioreactors for microalgal carbon dioxide sequestration offers the major advantages of increased microalgae productivity with controlled environmental conditions, and optimized space or volume utilization and, thus, more efficient use of costly land. Closed photobioreactors can more readily control environmental conditions (temperature, oxygen and nutrients) than open cultures. Although CO_2 from exhaust gases cannot be controlled because CO_2 is usually bubbled through the reactor with the excess CO_2 being emitted to the atmosphere, and the CO_2 concentration and temperature vary with the combustion conditions of the power plant.

5 Selection of Microalgae Species

Several thousands of species of microalgae exist. They can be grouped into four different categories:

(i) Cyanobacteria,
(ii) Rhodophytes,

(iii) Chlorophytes,
(iv) Chromophytes.

A considerable lot of these species have been effectively developed in photobioreactors to create an assortment of products. The most widely recognized species concentrated on are *Chlorella* sp. also, *Spirulina* sp., decided for their strength, profitability and non-toxicity (Fig. 3). Diverse microalgae species require distinctive living conditions (Borowitzka and Borowitzka 1988; Richmond 1999; Singh et al. 2005). A few algal groups favour more acidic conditions, as *Galderia* sp. also, *Viridella* sp., while others develop best in basic or somewhat neutral media, for example, *Chlorococcum and Synechococcus lividus*. The species that survive best in acidic conditions are for the most part more tolerant to high CO_2 fixations, since CO_2 brings down the pH of a solution (Table 2). The microalgae with the most limited doubling times, similar to Chlorella and Synechococcus lividus, are the ones with the most part higher profitability, essentially they become relatively speedier than different species.

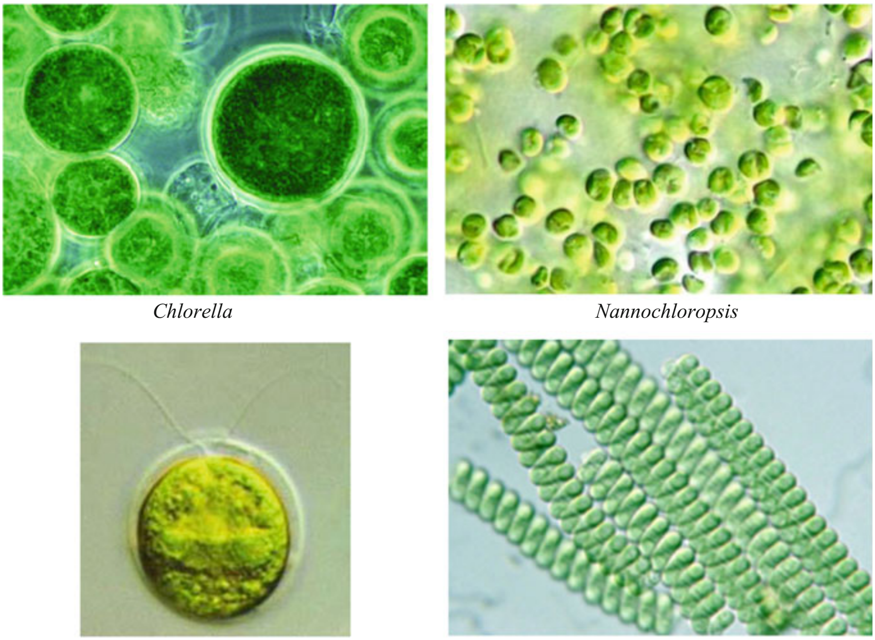
Chlorella *Nannochloropsis*
Chlamydomonas *Spirulina*

Fig. 3 Various microalgae: The most abundant natural source

Table 2 Co_2 tolerance of various species

Species	Known maximum CO_2 (%)	Concentration references
Cyanidium caldarium	100	Negoro et al. (1991)
Scendesmus species	80	Seckbach et al. (1971)
Chlorococcum littorale	60	Hanagata et al. (1992)
Synechococcus elongatus	60	Kodama et al. (1993)
Euglena gracilis	45	Miyairi (1995)
Chlorella species	40	Nakano et al. (1996)
Eudorina species	20	Nagase et al. (1998)
Nannochloris species	15	Yoshihara et al. (1996)
Spirulina species	10	Matsumoto et al. (1995)

6 Microalgae and Seaweed for CO_2 Fixation/Utilization

Microalgae are the potential source of food, feed, polymer and nutrients. It consumes 1.7–2 kg CO_2 to produce 1 kg biomass so it acts as good CO_2 scrubber. Algae biomass can be used as potential source for green fuel production, which will help the high energy demand of the world. Microalgae can be isolated from various diverse sources, including rivers, lakes and ponds, springs, soil and seawater, basically anywhere in the world Carbon dioxide from various industrial sources as power plants, chemical industries, etc. can be converted to biomass using algal mass culture pond systems (Amin 2009). The main advantage of using open pond systems is that the technology is very well understood and various commercial systems also exist. Algal pond systems are currently the most economic method to produce biomass on a large scale (Borowitzka and Borowitzka 1988; Sudhakar and Premalatha 2012a, b, c). Very high value products can be obtained from algal mass culture. Biological utilization of CO_2 using microalgae is an economically beneficial method to employ greenhouse gas emissions to generate value (Richmond 1999). Microalgae have a higher capacity for CO_2 utilization through photosynthesis than higher order plants, such as trees, shrubs and grasses. Microalgae are a diverse group of aquatic organisms and depending on the species they can produce different feedstock for energy generation (Sudhakar and Premalatha 2012a, b, c, 2015).

- Lipids for biodiesel and jet fuel production
- Carbohydrates for ethanol production
- Hydrocarbons and isoprenoids for gasoline production
- Hydrogen by direct synthesis in microalgae.

Beyond that the complete algal biomass can be processed for energy production. The different energy conversion paths for algal biomass include (Sudhakar and Premalatha 2012a, b, c)

- Gasification for syngas and BtL-production,
- Hydrothermal gasification for hydrogen production
- Methane production by anaerobic digestion
- Co-combustion for electricity production.

7 Carbon Dioxide Sequestration Through Photo-Bioreactors

Different Photobioreactors are designed and used for microalgae cultivation can be classified as open systems or closed systems. Open systems may be ponds, constructed on the large open areas, in rows with growth medium exposed to environment and sunlight. Closed systems are those where conditions are controlled. Closed system have many advantages over open system, as they can not be controlled easily and gets easily contaminated from external environment and could cause the microalgae mutate. Closed systems are easy to monitor, less chances of contamination occupy less space for the same algal growth. Closed system photobioreactor can be classified as follows:

- Tubular photobioreactors
- Mechanically stirred photobioreactors
- Airlift photobioreactors
- Bubble column photobioreactors.

8 Policy Framework for Carbon Dioxide Sequestration

Carbon capture and storage is a low-carbon technology that can form part of a balanced portfolio approach to address climate change, with advantages of economic and national security also. As of today, Carbon capture and storage is the only technology that may be able to achieve significant emissions reductions with 90% capture or even higher from existing fossil fuel infrastructure. Many studies have also suggested that unless Carbon capture and storage becomes a key part of a low-carbon technology portfolio; it is increasingly likely that energy-system carbon emissions will not be reduced to levels that limit global warming to 2 °C.

Initially, incentive policy at commercial scale needs to focus on trials of Carbon capture and storage, seeking information and cost-effective to make it possible to deploy Carbon capture and storage at reasonable scale and cost. The policy goal should not aim emissions reductions for their own sake, rather make advancement of Carbon capture and storage technology and establish commercial arrangements between storage technology, networks along with carbon capture. As Carbon capture and storage technology matures, it will become more familiar with the investors. Policy makers may either direct emissions savings where they believe them to be most cost-effective or simply let the market decide where to invest. The policy choices fall under four broad themes and the policy approach is likely to shift over time:

- Funding—incentives for operations as well as capital deployment
- Loss risks and the Cost—borne either by the private sector or public sector
- Penalties or the Subsidies—Penalizing emissions or subsidizing the abatement
- Support for technology—targeting Carbon capture and storage—specific incentives or technology-neutral incentives.

Although Carbon dioxide sequestration is not a perfect substitute for avoiding Carbon dioxide production because Carbon dioxide leaks back to the atmosphere and hence affects the future costs. The efficiency factor of Carbon dioxide sequestration can be expressed as the ratio of the avoided emissions to the economically equivalent amount of sequestered Carbon dioxide emissions.

Whether or not Carbon dioxide sequestration should be considered as a viable alternative to Carbon dioxide abatement is an open and much debated question (Kaiser 2000). Previous studies addressing Carbon dioxide sequestration develop elegant analytical expressions to analyze the trade-off between Carbon dioxide sequestration and Carbon dioxide abatement (Richards 1997; Van Kooten et al. 1997; Herzog et al. 2003) or analyze the optimal use of CO_2 sequestration in numerical models (Biggs et al. 2000; Lecocq and Chomitz 2001).

The range of risks along the innovation spectrum involved in commercializing Carbon capture and storage means that a portfolio of multiple policies is required which encompasses front-end and also back-end approaches. Government action with improved policies are required to both improve existing policy tools as well as should implement various newly improved mechanisms that would foster a market for Carbon capture and storage technology, such as policies that would require emissions reductions or directly establish a carbon price. A next generation policy portfolio would also need to reflect evolving political realities while also offering a longstanding solution that can hold up amidst political cycles and leadership changes. Though increased financial support certainly poses a political challenge, it is vital to continue to lower the costs of existing technologies along with finding and demonstrate new and cheaper technologies.

9 Value-Added Products

The absence of support structures, such as roots and stems, allows for a larger fraction of the microalgae to be used to create desired products compared to other types of biomass (Sudhakar et al. 2013). There is a broad range of valuable products that can be harvested from the production of biomass. The type and quality of product obtained depends on the species of microalgae, growing conditions and recovery methods implemented (Singh et al. 2005). The utilization areas of microalgae can be divided into three categories:

- Energy—production of substances such as hydrocarbons, hydrogen, methanol, etc.
- Foods and chemicals as carbohydrates, sugars proteins, oils and fats, sterols, alcohols, etc.
- Other chemicals as dyes, perfumes, vitamins/supplements, etc.

One type of microalgae, cyanobacteria or blue-green algae, has been studied extensively because of its many valuable products. The edible species include Nostoc, Spirulina and Aphanizomenon, which can be used as a raw, unprocessed food as they are rich in carotenoid, chlorophyll, phycocyanin, amino acids, minerals and bioactive compounds.

10 Major Problems

The major problems that companies face in implementing algae-based carbon dioxide sequestration techniques are as follows (Sudhakar et al. 2012a, b, 2013):

- The high cost of infrastructure
- Land space available is very less near power plants
- Uncertainty over public acceptance
- Specific operational problems as well as inefficiencies
- High CO_2 concentrations cause the algae suspension to become acidic, thereby stunting algae growth.

11 Conclusion

In this study, it was determined that CO_2 fixation using micro algal species is very promising and competing alternative technologies to conventional sequestration. The various aspects associated with the design of microalgae production units (photobioreactors and open ponds) are to be studied in detail due to the flue gas processing (e.g. mercury, arsenic and particulate removal, etc.) that must be performed prior to exploitation; CO_2 utilization directly from a coal-fired power plant is not currently feasible with the available technologies. Despite only a small percentage of CO_2 being utilized when compared to the total amount emitted by a 500 MW power plant, CO_2 sequestration by microalgae is recommended for the creation of value from CO_2. Microalgae cultivation for CO_2 sequestration is more feasible than geological sequestration; it helps in maintaining environmental balance thus reducing the threat of global warming.

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Chapter 11
Clathrate Hydrates: A Powerful Tool to Mitigate Greenhouse Gas

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Abstract Adsorbents like zeolites, metal-organic materials (MOM), porous polymers, metal oxides, carbonaceous materials (CM) and porous silica, etc. are being investigated for CO_2 capture/storage. Contemporary literature reports highest CO_2 adsorption capacity in MOMs, e.g. MOF-200 and MOF-177 as 54.5 mmol g^{-1} (at 5 MPa and 298 K) and 33.5 mmol g^{-1} (at 3.5 MPa and 298 K), respectively; and it is 46.9 mmol g^{-1} for CM. Noticeable drawbacks, however, are hard to synthesise and expensive; sensitive to moisture; issues with activation, regeneration and recycling of sorbent materials, etc. Ideal material for CCS should be cheaper, robust for recycling, good thermal and structural stability towards moisture. Although the other materials can fulfil some conditions, e.g. recyclable, thermal and structural stability, etc. but their CO_2 adsorption capacity is significantly low. The gas hydrates on the other hand have proven to be useful and economical alternative for gas separation and storage/sequestration. In the present set of experiments, we demonstrate that the CO_2 storage capacity is 29.7 g^{-1}, in hydrates, formed from water trapped in the voids of SiO_2.

Keywords Clathrate hydrates · Greenhouse gas · CO_2 storage · Silica powders

Abbreviations

MOM	Metal-organic materials
CM	Carbonaceous materials
GH	Gas hydrates
STP	Standard temperature and pressure
TEOS	Tetraethyl orthosilicate
FTIR	Fourier transform infrared spectroscopy

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R_w	Ratio of water to matrix
SDS	Sodium dodecyl sulfate
MOF	Metal organic frameworks

1 Introduction

Increasing levels of greenhouse gases such as carbon dioxide, methane, etc. in the atmosphere is currently of great concern. In order to meet the increasing energy demands, both the developed and the developing countries will continue to rely heavily on the use of fossil fuels, thus continuously increasing the accumulation of greenhouse gases in the atmosphere. Thus, alarming need is to look for the ways for striking a balance between meeting the energy demands and managing the levels of greenhouse gas emissions. *Carbon dioxide (CO_2) capture and storage/sequestration (CCS) is a process consisting of the separation of CO_2 gas from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere.* Most commonly examined methodologies for longer time storage are geological storage—in gas/oil fields, coal mine, ocean sequestration—direct injection and mineral carbonation—in various geological formations and biosequestration, etc. On the other hand, hydrate-based technology plays a pivotal role at each step, especially for gas separation, storage and transportation, and the process itself has been critically challenged by slower formation rate and lower conversion efficiency of gas to solid hydrate, resulting in insufficient storage capacity. Addition of some thermodynamic promoters (Chari et al. 2011) and/or surfactants (Zhong and Rogers 2000); or usage of porous medium fully or partly saturated with water to the hydrate system has proven to provide plausible solution for attaining higher and rapid conversion into hydrate phase (Prasad et al. 2012; Carter et al. 2010). In a series of laboratory experiments, we established the usefulness of low density (hollow) silica as a matrix material for achieving higher and rapid hydrate conversions with appreciable recycling capacity (Chari et al. 2013a; Prasad et al. 2014a, b).

Gas hydrates (GH), also known as clathrate hydrates, are non-stoichiometric inclusion compounds, in which gaseous guest molecules are trapped in a host lattice, formed by water molecules in an ice-like hydrogen-bonded framework. Essential conditions for its formation and stability are enough supply of host (water) and guest (of suitable size) molecules, and moderately higher pressure and sub-ambient temperature. Such conditions usually exist in certain permafrost and top layers of ocean bottom sediments; and therefore the gas hydrates with natural gaseous molecules such as methane, ethane, propane, etc. as guests are often found in such conditions. They considered as future energy source because a large fraction (160–180 cm^3 (STP) cm^{-3}) of guest molecules are contained in this form. The molecular size for methane and carbon dioxide are similar and they crystallize into cubic structure with space group *Pm3n*. Its unit cell consists of 46 water molecules forming eight (two pentagonal dodecahedron 5^{12} and six tetrakaidecahedron $5^{12}6^{2}$) cages. The ideal amount of CO_2 in hydrates is 29.83 wt% (6.66 mmol g^{-1}) when all the cages are filled, while it is 24.17 wt% (5.50 mmol g^{-1}) when only $5^{12}6^{2}$ cages are filled.

There is paradigm shift in mitigating the emissions of CO_2 not only as greenhouse gas, but also as useful raw material in manufacturing certain agro products and chemicals. Therefore, materials are being developed aiming to capture larger fractions of CO_2 from its source locations. Various types of adsorbents like zeolites (Jee and Sholl 2009; Zukal et al. 2012), Metal-organic materials (MOMs) (Millward and Yaghi 2005; Liu et al. 2012), porous polymers (Rabbani and El-Kaderi 2012; Ben et al. 2009), metal oxides (Koirala et al. 2011; Broda and Miiller 2012), carbonaceous materials (Silvestre-Albero et al. 2011; Zhou et al. 2012) and porous silica (Ren et al. 2012; Yu et al. 2012), etc. are presently being investigated for CO_2 capture/storage. The highest CO_2 adsorption capacity for MOMs, e.g. MOF-200 and MOF-177 it is 54.5 mmol g^{-1} (at 5 MPa and 298 K) (Furukawa et al. 2010) and 33.5 mmol g^{-1} (at 3.5 MPa and 298 K) (Piotr et al. 2010), respectively. However, some of the associated drawbacks with them in practice are hard to synthesise and expensive; sensitive to moisture; issues with activation, regeneration and recycling of sorbent materials, etc. Specially prepared carbonaceous materials (carbon molecular sieves) have also shown higher adsorption capacity for CO_2 (46.9 mmol g^{-1} at 5 MPa and 298 K and 24.2 mmol g^{-1} at 3.5 MPa and 298 K) (Silvestre-Albero et al. 2011). For CCS applications ideally the desired material should be cheaper, robust for recycling, good thermal and structural stability towards moisture. Although the other materials can fulfil some conditions, e.g. recyclable, thermal and structural stability, etc. but their CO_2 adsorption capacity is very low. It is 4.27 mmol g^{-1} for amine functionalised zeolites with 7% water vapour (Su et al. 2010) and 1.25 mmol g^{-1} in metal oxide modified with organic ligands (Wang et al. 2012). The gas hydrates on the other hand have proven to be useful and economically adoptable alternative for gas separation and storage/sequestration. In the present report, we present our experimental results on CO_2 retention capacity in different silica (SiO_2) saturated with H_2O.

2 Experimental Section

2.1 *Materials and Characterization*

We used five types of SiO_2 samples as water/hydrate adsorbents and their density, grain size and surface area details are shown in Table 1. Two of them (hollow silica—b and solid silica—b) were synthesized in the laboratory using the procedure described in the literature (Jee and Sholl 2009). Briefly the hollow silica is prepared by the hydrolysis of SiF_4 gas obtained by reacting Na_2SiF_6, SiO_2 and H_2SO_4

at 220–240 °C. On the other hand, solid silica was prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol and water medium in the presence ammonium hydroxide. Another two silica samples (hollow silica—a & solid silica—a) were obtained from Nanoshel (M/S Intelligent Materials Pvt. Ltd.) and these are the same samples that were used in our earlier study (Prasad et al. 2014a, b; Chari et al. 2013b). Fifth sample was purchased from M/S Sigma Aldrich Company (CAS# 7631-86-9) and was used as received. De-ionized ultra-pure water (Millipore—type 1) was used, and the dissolved gases were removed by evacuation.

Molecular spectroscopic techniques are used to identify the mineral composition and the purity of the sample. We have used Fourier Transform Infrared Spectroscopy (FTIR) to identify the silica compositions. Figure 1 shows the

Table 1 Table describing the textural properties of silica material synthesised under various conditions

Sample	Density (g/cm^3)	Particle size	BET surface area (m^2/g)
Hollow silica—a	0.0125	20–70 µm	2.31
Hollow silica—b	0.06	200 nm	2.8669
Solid silica—a	1.35	20–70 µm	
Solid silica—b	>1	60–70 nm	182.3956
Aldrich silica	2.4	5–15 nm	620

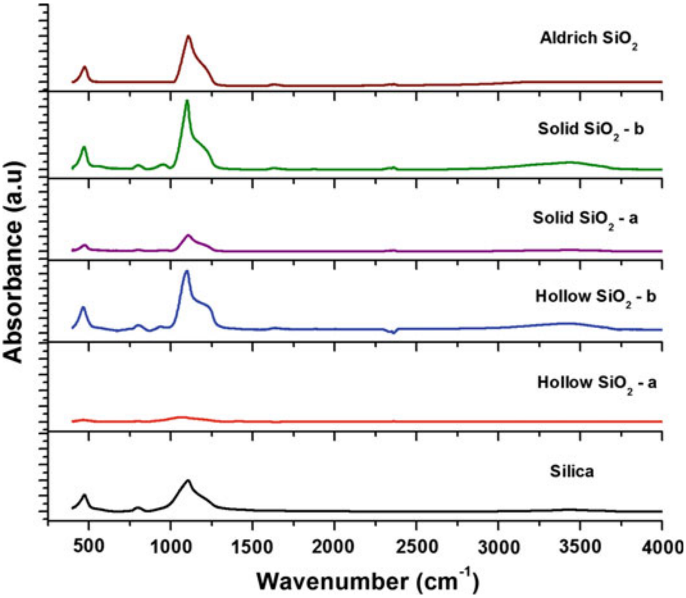

Fig. 1 FTIR spectrum of different silica samples is compared with the silica spectrum from NICOLET-NEXUS library (*bottom*)

chemical purity of the samples which were characterized by the FTIR, and it was found to be 95%. The FTIR spectrum of silica samples with peaks at 490 cm^{-1} (Si–O), 800 and 1090 cm^{-1} (Si–O–Si) and the closest match is for silica of Nicolet library. Absence of sharper mode around 3600 cm^{-1} indicates nonexistence of silinol (Si–OH) group.

2.2 *Experimental Setup*

Figure 2 shows the schematic of the experimental set up where the main part was a SS-316 cylindrical vessel, which can withstand gas pressures up to 15 MPa, and volume of the vessel was 250 mL (non-stirred). A cold fluid (water + glycol mixture) was circulated around the vessel with the help of a circulator to bring and maintain temperature inside the cell at a desired level. A platinum resistance thermometer (Pt100) was inserted into the vessel to measure temperature with an accuracy of ±0.5 K, while pressure in the vessel was measured with a pressure transducer (WIKA, type A-10 for pressure range 0–25 MPa with ±0.5% accuracy).

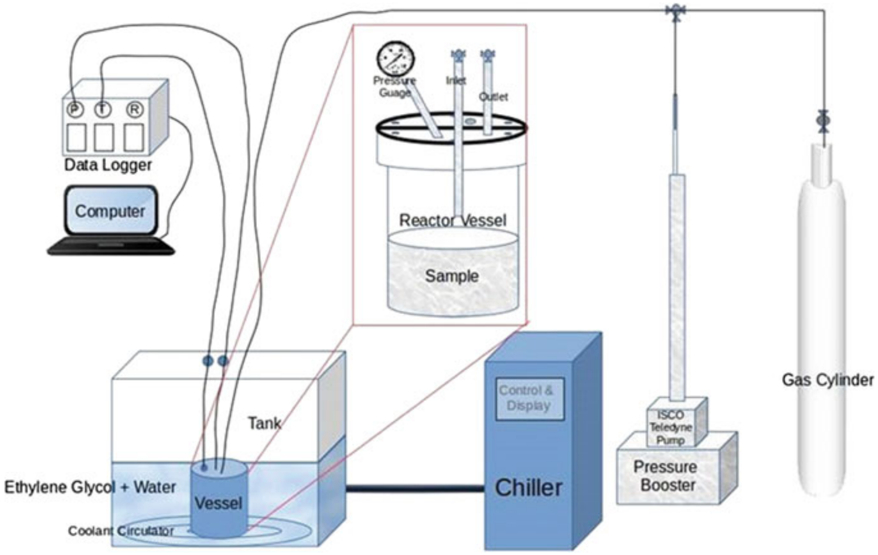

Fig. 2 The experimental apparatus used for the CO_2 hydrate formation in the non-stirred reactor

2.3 Methodology

A fixed amount of silica powder was mixed with variable amounts of water and the resulting mixtures were pressurized (@300 K) with carbon dioxide gas (99.5% purity) in all the experiments to synthesize hydrates. Silica and water were mixed thoroughly in the reactor with the help of a glass rod, and no rigorous blending was applied. The atmospheric gases in the experimental cell were diluted by purging with methane gas prior to the experiments and methane gas was filled to the desired level using the Teledyne ISCO syringe pump to a pressure and temperature outside of the hydrate stability zone. Then, the reactor was isolated from the ISCO pump/gas tank by closing the gas inlet valve. Subsequently, a cold fluid from the chiller was circulated to bring down the temperature of the reactor and hydrate formation was detected by a sharp pressure drop at a particular temperature. However, the system has taken some time (approximately 30–70 min) to reach into the gas hydrate stability zone for nucleation, and it appears that is dependent on the initial driving force and the silica to water ratio. The insignificant head-pressure drop in the reactor observed over a longer duration indicates saturation in hydrate conversion. The temperature and pressure were logged for every 60 s of the time interval. The molar concentration of methane gas (ΔnH, t) in the hydrate phase during the experiment at time t is defined by the following equation:

$$\Delta nH,\ t = ng, 0 - ng, t = (P_0 V / Z_0 R T_0) - (P_t V / Z_t R T_t), \qquad (1)$$

where Z is the compressibility factor calculated by the Peng–Robinson equation of state. The gas volume (V) was assumed as being constant during the experiments, i.e. volume changes due to phase transitions were neglected. ng, 0 and ng, t represent the number of moles of feed CO_2 gas at 280 K taken at zero time and in the gas phase at time t, respectively. The hydrate yield was computed from the observed CO_2 gas consumption to the expected values with ideal stoichiometric compositions ($8CO_2 \cdot 46H_2O$) (Chari et al. 2013c). In literature, different authors have used different hydration numbers in the range of 5.75–6.1, and this variation has been mainly attributed due to the cage occupancy factors (Sloan and Koh 2008). Throughout this study, we have used the ideal hydration number (5.75) assuming full occupancy of the cages. In the process, we underestimate the hydrate yield about 5%.

3 Results and Discussions

Earlier experiments reveal that the water to hydrate conversion is appreciably large in the presence porous medium. In order to store more gas in the form of hydrates one another requirement is the presence of more amount of water. However, the hydrate conversion critically depends on the degree of pore water saturation

(R_w = ratio of water to matrix) and for silica matrix the ratio is much smaller than one. In the present study, we noticed that the value of R_w vary significantly from sample to sample. We used nearly same amount of water (16–22 g) in all the experiments and our goal is to avoid formation of thick paste or slurry using excess water.

In Fig. 3, we show the p–T trajectories during a formation and dissociation cycle. Corresponding temporal variations in temperature and amount of gas consumed during hydrate formation cycle are plotted in Fig. 4. The p–T trajectories depict the finger print signatures of hydrate conversion process in a typical isochoric process. A sudden drop in the head-pressure clearly shows the state change to hydrates when the temperature is within the hydrate stability region. On the other hand, a study decrease in the head-pressure outside hydrate stable region with temperature could be due to gas dissolution/adsorption on dry silica grains. A similar linear variation at lower temperatures inside the hydrate stable region

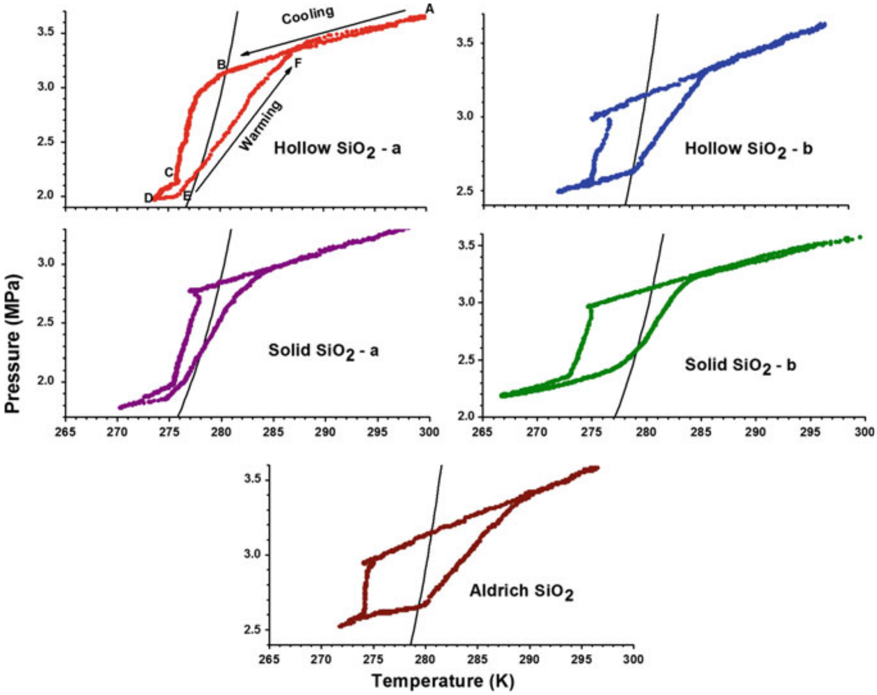

Fig. 3 The pressure–temperature trajectories showing the formation and dissociation of CO_2 hydrate synthesized in non-stirred reactor in all the systems. The *solid black line* is the phase boundary curve for sI CO_2 hydrate computed using CSMGem. *Arrow* marks in the p–T trajectory of hollow SiO_2—a shows the cooling during hydrate formation and warming during hydrate dissociation of the system. Points *A*, *B*, *C*, *D*, *E* and *F* indicate the cooling start, nucleation start, formation end, warming start, dissociation start and dissociation end. This is same for remaining systems

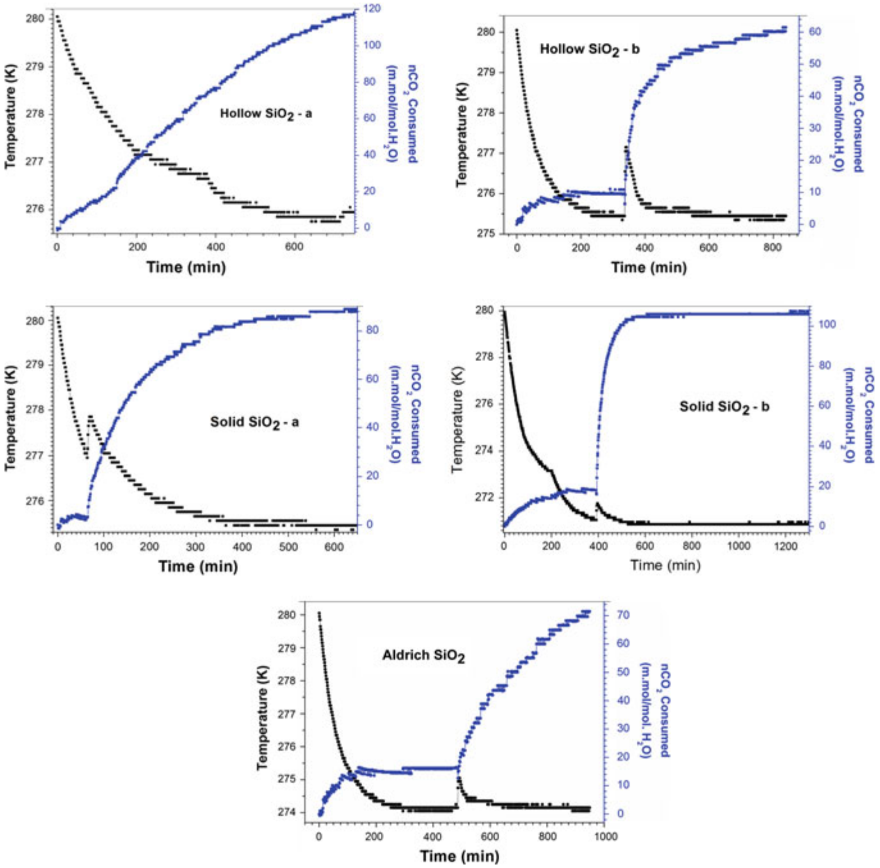

Fig. 4 Consumption of CO_2 gas and corresponding temperature rise during nucleation start in the reactor vessel as a function of time in the different silica suspensions (*black solid line* corresponds to temperature variation with time and *blue solid line* corresponds to gas consumed with time)

indicates an apparent saturation in the water to hydrate conversion. All hydrates formation experiments were conducted for 15–20 h duration to ensure the saturation of the process.

Observed temporal variations in the temperature and the remnant CO_2 pressure provide much useful information on hydrate conversion process. The water to hydrate formation is an exothermic process and normally a temperature spike is often associated with nucleation phenomenon. Hydrate nucleation event is clearly seen in the temperature range 275–277 K, following which rapid gas consumption has been occurred (Fig. 4) in all the samples, indicating the growth of hydrates. It is relatively easy to estimate the induction time in such cases. The induction time usually is defined as the time lapsed until the occurrences of hydrate nucleation event when the system is well within hydrate stable zone.

In Table 2, we show the observed induction times in SiO_2 matrix and the time zero in our observations is at 280 K. As shown the induction time varies significantly from sample to sample. Similar observations have earlier been reported by Linga et al. (Linga et al. 2012) and Kumar et al. (2015) Further, Kumar et al. (2015) have used kinetic promoter (SDS—1 wt% sodium dodecyl sulfate) along with silica sand or silica gel to reduce the induction time typically by an order of magnitude. It is well known that the induction time depends on several factors such as operating conditions (*p* or *T*) and history of water. Usually the hydrate formation is relatively quicker in "memory" waters (the water with hydrate formation and dissociation history) than in pristine water. As shown in Table 2 and in Fig. 4, the induction time is estimated as the time taken by the system (from 280 K) until appearance of a sharp exothermic temperature peak, indicative of hydrate formation. It is varying between 225 and 490 min depending on the type of silica matrix.

Another important factor is the overall hydrate conversion from water–CO_2 system so as to trap more amount of CO_2 gas in the form of hydrates. It has been established that the addition of some porous material will certainly help in achieving higher hydrate conversions. Further, earlier studies have shown that the degree of water saturation also play an important factor in hydrate conversion. Excess amount of water prevents the hydrates conversion. Accordingly we used various types of silica powders as matrix materials along with optimum levels of water; and observed significant CO_2 hydrate conversions in shorter (400 min) durations after nucleation. As noted in Table 2, the hydrate conversion varies in the range 84.5–40.5%. The present results are in agreement with the literature results obtained using water saturated silica bed. Still higher hydrate conversions, particularly in samples (hollow silica—b) and aldrich silica, could be possible by optimizing sample volume/experimental time. In the present study our primary goal is to use similar amount of water to investigate the CO_2 storage capacity in the form of hydrates and therefore we used 250 mL reactor. Based on visual observations we

Table 2 Experimentally observed CO_2 gas consumption during hydrate formation in suspensions of different silica particles and the calculated amount of CO_2 gas stored per gram SiO_2 during hydrate formation in different systems

Sample	R_w = wt. H_2O/wt.SiO_2	Induction time (min)	Consumed CO_2 (mol)	Yield %	Stored CO_2 (/g)
Hollow SiO_2—a	4	–	0.154	84.5	27.7
Hollow SiO_2—b	10	320	0.066	42.5	29.7
Solid SiO_2—a	2	225	0.112	61.5	5.6
Solid SiO_2—b	2	–	0.088	59.6	9.8
Aldrich SiO_2	1.6	490	0.050	40.5	5.6

noticed that the apparent water saturation factor also varied significantly (see Table 2). This factor is significantly high for hollow silica samples, whose bulk density is lower (<1 g/cc). A relevant parameter to compare the CO_2 storage in porous materials in the form of hydrates is the amount of gas stored per mol water per gram material. Using this parameter one can compare the storage capacity with other materials such as MOMs, Zeolites, etc. As shown in Table 2, this parameter is lower (5.6–9.8) for samples with bulk density larger than one. On the other hand, it is significantly high (27.7–29.7) for lesser dense silica samples. As described along the manuscript, the best adsorption capacity reported in MOMs and carbonaceous materials is 33.9 mmol g^{-1} (@ 3.5 MPa).

In the present study, the gas trapping mechanism is through hydrate formation and therefore we conducted all the experiments at sub-ambient (closer to ice melting) temperatures and the gas pressure close to 3.5 MPa pressure. It is possible to optimize the experimental parameters such as size of the reactors and other operative conditions such as p, T, R_w so as to achieve higher hydrate to water conversion. Striking advantage of the present study is the inexpensive and ease in the preparation of matrix materials silica. Further, we demonstrated the possibility of conducting the experiments in gram scale. Whereas, the experiments using MOMs, activated carbonaceous materials or zeolites were conducted in small size reactors using milli-gram samples.

4 Conclusions

In summary, we demonstrate the usefulness of clathrate hydrate-based technology in capturing/storing the CO_2 gas as guest molecules. It is illustrated that the process of hydrate conversion is efficient in water saturated silica systems. The overall CO_2 storage capacity (mmol CO_2/mol H_2O/g SiO_2) is extremely high (27.7–29.7) in low density silica matrix and the same is comparable to other materials such as, MOF-200, MOF-177 and specially prepared CM under similar CO_2 pressure conditions. However, the advantage with low density silica is the absence of rigorous preparative methodology and higher thermal stability. The storage capacity of these materials can be improved further by optimizing the water adsorption on dry silica and hydrate formation conditions.

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Chapter 12
Carbon Sequestration and Utilization—India's Energy Woes

Gautam Sen

Abstract India has approximately 0.5% of world's Oil and Gas reserves and fifth highest coal reserves in the world. Renewables like solar, hydropower and wind are in plenty but considering the state of the technology and commercial issues, renewables can only make a significant contribution to India's energy basket in the mid- to long term. Most of our power plants are coal-based and power requirements are growing exponentially. Energy analysts believe that in spite of huge coal reserves, India may overtake China and be the world's highest importer of coal. It is therefore imperative that we start adopting clean coal technology. Carbon dioxide sequestration is one such technology where carbon dioxide emitted in power plants is captured and reinjected into the subsurface either in depleted oil, gas fields or coal seams or even in plain saline aquifers so that it remains entrapped. Carbon dioxide sequestration is also used as a tertiary recovery process to enhance recovery factor in discovered oil fields, both for light and heavy oil. USA, Canada and Brazil are champions in enhanced oil recovery projects through carbon sequestration with more than hundreds of projects worldwide. Sequestration in saline aquifers is relatively new and besides USA and Canada, South Africa has commenced a pilot project. Algeria is also exploring feasibility of using depleted gas fields for sequestration. Porosity, permeability, volume of reservoir and seal are the critical parameters for success of sequestration in a saline reservoir. China is the first country in Asia to take up sequestration in saline aquifers and is carrying out research and modelling work in a large scale to ensure technical feasibility. Enhanced coal-based methane production through carbon dioxide sequestration is an area of active global research. Coal rocks have higher affinity for carbon dioxide; hence methane is displaced increasing its mobility. Coal-based methane production is however low at present. This paper describes carbon dioxide utilization challenges for enhanced oil recovery, sequestration in saline aquifers and the success in Iceland on storing carbon dioxide within basalts. Reservoir modelling and simu-

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lation studies on the specific host reservoir rock have to be carried out before large volumes of carbon dioxide can be reinjected and stored in the subsurface.

Keywords Saline aquifers · Sedimentary basins · Acoustic and elastic impedance · Pre stack seismic inversion · Hyaloclastites · Flood basalts

Abbreviations

NELP	New Exploration Licensing Policy
ONGC	Oil and Natural Gas Corporation
OIL	Oil India Limited
TCF	Trillion cubic feet
WAG	Water alternating gas
3D	Three dimensional

1 Introduction

India is poised for a major economic growth but unfortunately it is not favourably endowed in its hydrocarbon resources. Ever since liberalization of our oil industry and oil price escalation in the last two decades, both public and private upstream players have spent billions of dollars in oil and gas hunt across India's deep and shallow waters and onshore. Besides a major oil and gas discovery in Mangla field and surrounding areas in Barmer district Rajasthan in the Pre-New Exploration Licensing Policy (NELP) and gas discoveries in deep waters in Godavari in the NELP rounds announced have yielded very little dividends. It is time that we accept that prospective areas for conventional oil and gas in India are limited in the country. Recent exploration failures have proved that Bay of Bengal is not North Sea and petroleum system has not developed in India's deep waters in west coast. There are small- to mid-size discoveries in Krishna-Godavari and Cauvery deep waters and in NEC blocks in Mahanadi which are areas for future development but at best they will prolong the decline curve in indigenous oil and gas production. Besides fields in Barmer and Krishna-Godavari deep water, the producible oil and gas fields are those that were discovered by Oil & Natural Gas Corporation (ONGC) and Oil India Limited (OIL) in sixties, seventies and eighties. The present dispensation has recently announced rational, attractive and more transparent policies to attract players to invest in Indian acreages, but it is the perceived prospectively which attracts.

On the other hand, Shale gas reserves in India are in tens of trillion cubic feet (TCF) but its extraction involves requirement of vast areas of land and fresh water which is challenging in Indian conditions. There are also other environmental factors to be considered. Except few sparsely populated areas within the prospective zones, Shale Gas extraction may not be feasible unlike other parts of the world. As a result, India imports over 80% of its oil requirement and this is projected to touch 90% in foreseeable future. ONGC Videsh limited is vigorously hunting for global oil and gas acreage not only as an investor with participating interest but are also global operators singly or jointly. But it is anybody's guess whether equity oil is really an answer to energy security in the present market conditions. International presence has its own advantages in building indigenous technical and managerial capabilities and the recent deals in Russia and in Iran under government to government negotiation is a testimony to it.

2 Global Oil and Gas Scenario

High oil prices in the last two decades till recent past and major technological breakthroughs enabled exploration in frontier and logistically challenging areas globally, besides enhancing recovery factor of discovered oil. This led to accretion of reserves which are greater than oil production in this period. Today the world has higher producible reserves than what it had two decades ago and the world is heading towards a peak demand and not peak oil as was postulated earlier. There has been recent glut in oil supply and all storage tankers are selling at a premium in spite of low oil prices. China has made large-scale efforts to build internal strategic reserves. Low oil price is the outcome of many factors, like slowdown in economic growth globally, higher energy efficiency, shale oil production and gas revolution, and ecological consideration promoting gas-based industry wherever feasible at the expense of oil and coal besides geopolitical factors. Finding and development cost even for conventional oil and gas fields varies widely from basin to basin, depending on the volumes, depth of occurrence, geological complexity, logistics, etc. Most of the middle East OPEC countries enjoy the lowest producing costs and are affected only in the reduction of profits by oil price crash. Neither they nor Russia which are the main producers are willing to cut down their production to prevent the glut for fear of losing their market share.

The recent plunge in oil price is changing the rules of the game. Exploration in frontier areas has come to a standstill. Low oil price also ensures that Shale Oil and Gas extraction becomes financially unviable. Unconventional heavy oil extraction in Venezuela, Canada's tar sands project has taken a serious hit. Companies are cutting down their staff and lacs of knowledge workers have been laid off in the last two years. Industry analysts predict that if this trend continues Middle East's domination in oil reserves which was a thing of the past, it will again haunt global politics. Luckily in the last three months, oil prices are picking up but it is very unlikely that it will touch anywhere near its earlier high.

It is in the interest of both the consumers and the industry that oil prices should be high enough to ensure financial sustainability of the industry players, permit exploration in frontier areas so that globally reserve replenishment ratio is higher than unity minimizing hegemony of any region and be low enough for the comfort of the consumers.

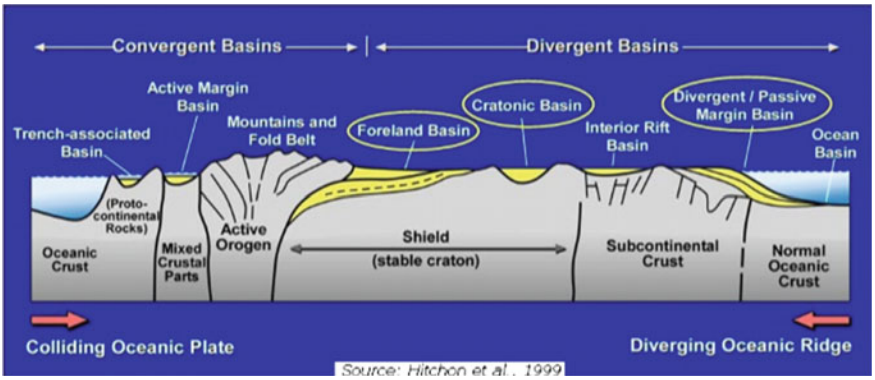
3 Domestic Coal

India's coal reserves have the highest reserves to production ratio as compared to other fossil fuels, i.e. oil and gas but because of indigenous coal quality with high ash content and our industry's over dependence on coal, India is also projected to be the world's highest coal importer. More than 65% of India's electricity generation capacity comes from thermal power plants, with about 85% of the country's thermal power generation being coal-based. The 10 biggest thermal power stations operating in India are all coal-fired. Thermal power plants are the main source which generates carbon dioxide and flue gases. Carbon dioxide sequestration entails capturing these gases and reinjecting into the subsurface at depths usually greater than a km within sedimentary basins. Incentives are being given to boost renewables energy production which is eco-friendly and sustainable and this can serve the country well in long term but in the short- to mid-term they can only supplement the energy requirement.

4 Carbon Dioxide Sequestration and Sedimentary Basins

Sedimentary basins across the globe are the habitat for oil and gas fields, saline aquifers and coal seams. Basin is a depocentre in the Earth's crust formed due to tectonic forces either in extensional or compressional or in strike slip regime. A pictorial diagram is shown in Fig. 1 describing the various geological set ups in which basins evolve primarily due to plate tectonics (Hovorka and Tinker 2010) and lithospheric stretching of continental plates.

Sedimentary rocks transported from highlands by water system deposits in this basin and the process continues with increased subsidence either by gravity or by renewed tectonic activity. In situ, organic growth of carbonate reefs besides



Source: Hitchon et al., 1999

Fig. 1 Cross-sectional representation of various types of sedimentary basin deposition of limestone in stable shelf areas occurs under favourable environment. Sandstone, and limestone rocks usually have pores and they are either filled with saline aquifers or in some cases hydrocarbons. Coal is deposited in sedimentary basins when plants and trees were buried in swampy conditions. Coal seams can entrap fluids particularly methane. It is important that these fluids do not escape back into the atmosphere and therefore top and lateral seals are necessary and usually impermeable rocks like shale/salts/evaporites or tight limestone provide seal. Depleted oil, gas fields, coal seams and saline aquifers within a sedimentary basin can be ideal locales for pollutant gases in case they are injected into the subsurface. Care needs to be taken to ensure that sealing mechanism is not disturbed in old oil fields and they exist in sedimentary basins which are known to host saline aquifers.

There can be four different situations where carbon dioxide is injected into the subsurface (Stephen 2012):

- injected into a zone that contains hydrocarbons (of which oil is the target) and brine; CO_2, and commercially significant oil are produced.
- injected into hydrocarbon reservoirs similar to CO_2-EOR reservoirs (originally containing gas and or oil) but without extraction of any oil.
- injected into a formation that lacks any commercially significant hydrocarbons; brine could be produced to manage the process.
- Injected into brine formations or hydrocarbon reservoirs in combination with other processes, such as methane or heat extraction.

4.1 Enhanced Oil Recovery

Enhanced oil recovery technique using carbon dioxide is a tertiary recovery method after natural depletion and water injection methods have been applied to the oil field. This technique has been in vogue for the last four decades with USA having the largest number of projects. After identifying oil reservoirs suitable for enhanced oil recovery through carbon dioxide sequestration, efficient flooding process is designed and implemented. Carbon dioxide is injected into an oil bearing stratum under high pressure. Miscible CO_2 interacts with the reservoir oil resulting in low viscosity, low interfacial tension (Goel et al. 2015) and therefore higher mobility. This therefore reduces the residual oil saturation. The challenge is to increase area of contact of the two phases. In case of immiscible CO_2 with reservoir oil, due to low reservoir pressure or heavy or too light oil, mobility still increases due to oil phase swelling and viscosity reduction of the mixture in some instances. CO_2 produced along with hydrocarbon particularly in miscible case is separated and recycled back into the oil reservoir. Recent changes in EOR technology incorporate very large volume of injected carbon dioxide, better mobility control through alternate use of gas and water, advanced and optimized infill well drilling and completion to target reservoir above oil water contact and bypassed oil zones left unswept during the secondary water injection stage. Table 1 illustrates some of the

Table 1 Examples of DOE sponsored CO_2 sequestration projects in the U.S. involving EOR

EOR field	CO_2 source	Geological stratum	Injection start date	Cumulative CO_2 injection	Description
Zama Field, Alberta, Canada	Natural gas processing plant	Pinnacle roof, middle Devonian Keg River	December 2006	230,000 tonnes	The Zama of field validation test being conducted in Alberta, Canada, is evaluating the potential for geologic sequestration of CO_2 in an acid gas stream that also includes high concentrations of hydrogen sulphide (H_2S) for concurrent purposes of CO_2 sequestration, (H_2S) disposal, and EOR. The acid gas is generated as a by product during the processing of raw natural gas being extracted from the field
Williston basin	Pulverized coal power plant	Devo Duperow or Mississippian Madison group	2011	500,000 tonnes/year	The Williston Basin demonstration test will evaluate the potential for geological sequestration of CO_2 in a deep carbonate reservoir for the deal purpose of CO_2 sequestration and EOR Characterization studies indicate that the oil fields of the Williston basin may have over 1 billion tones of CO_2 storage capacity. Additionally, the Volume of in incremental of that could be produced from Williston Basin oil fields has been estimated to be approximately 1 Billion barrels
Louden fields, *Illinois*	Refinery or ethanol plant	Mississippian Weider sandstone	March 2007	43 tones	The Louden fields test, an enhanced oil recovery “huff-n-puff” project, is designed to inject (huff) CO_2 into a producing well for 3–5 days, allow the gas to soak for approximately one week, then place the well back on production and measure the amount of petroleum fluids produced (puff)
Louden fields, *Illinois*	Refinery or ethanol plant	Mississippian Weider sandstone	February 2008	2500 tonnes	The well conversion EOR fields test does not require the drilling of any new wells because available well(s) will be converted to handle CO_2 injection and the pattern and spacing of existing wells is adequate to test EOR processes in the reservoir, well conversion represents a potential near term, low cost opportunity to implement EOR
Snyder, Permian basin, Texas	McElmo Dome	Strawn—and Canton- age carbonate reefs	Second quarter 2008	700,000 tonnes	This test will include a post—audit modelling analysis of injected CO_2 for EOR over the last 30 years at the SACROC unit in the Permian basin of Texas, in addition to intense monitoring analyses of ongoing CO_2 injection at SACROC
Aneth oil fields, bluff, Utah	McElmo Dome	Paradox formation, Pennsylvanian desert Creek	Second quarter 2007	300,000 tonnes	The primary research objective of this EOR. Sequestration test is to evaluation and maximize the efficacy of CO_2 subsurface monitoring technologies, and to improve the ability to track the fate of injected CO_2 and to calculate ultimate storage capacity
Weyburn, Saskatchewan	Dakota gasification plant	The Midale beds of the Mississippian Charles formation	September 2000	33 million tonnes	The Weyburn program is organized around five technical themes; geological Integrity, wellbore integrity, storage monitoring methods, risk assessment and storage mechanism, and data validation and management. The technical objectives are to determine the long—term storage risks and monitoring requirements to mitigate such risks

DOE sponsored EOR projects in USA (NETL 2010) and effects of long-term geological storage of carbon dioxide.

Depending on the reservoir geology, fluid and rock properties, timing relative to water flooding, and well-pattern configuration, the CO_2-EOR flood may use one of several recovery methods as described below (Verma 2015):

I. Continuous CO_2 injection: This process requires continuous injection of a predetermined volume of CO_2 with no other fluid. Sometimes a lighter gas, such as nitrogen, follows CO_2 injection to maximize gravity segregation. This approach is implemented after primary recovery and is generally suitable for gravity drainage of reservoirs with medium to light oil as well as reservoirs that are strongly water-wet or are sensitive to water flooding.

II. Continuous CO_2 injection followed with water: This process is the same as the continuous CO_2 injection process except for chase water that follows the total injected CO_2 slug volume. This process works well in reservoirs of low permeability or moderately homogenous reservoirs.

III. Conventional water-alternating-gas (WAG) followed with water: In this process, a predetermined volume of CO_2 is injected in cycles alternating with equal volumes of water. The water alternating with CO_2 injection helps overcome the gas override and reduces the CO_2 channelling thereby improving overall CO_2 sweep efficiency. This process is suitable for most of the reservoirs with permeability contrasts among various layers.

IV. Tapered WAG: This design is similar in concept to the conventional WAG but with gradual reduction in the injected CO_2 volume relative to the water volume. With an objective to improve CO_2 utilization, tapered WAG is the method most widely used today because this design improves the efficiency of the flood and prevents early breakthrough of the CO_2, thus less recycled CO_2 and better oil recoveries.

V. WAG followed with gas: This process is a conventional WAG process followed by a chase of less expensive gas (for example air or nitrogen) after the full CO_2 slug volume has been injected.

Indian Oil fields are located in Gujarat, Rajasthan, Assam, Andhra Pradesh and Tamil Nadu in on land areas while most of the power plants are in eastern and central India. Possibly because of distant locations as well as different agencies which control Coal. Power and Oil, EOR processes using CO_2 have not been implemented commercially in India. Since the technology is well documented, commercial testing in key oil fields may also be attempted to enhance oil recovery through sequestering carbon dioxide. Even if the process does not lead to an improvement in recovery factor, yet a large fraction of the volume of injected carbon dioxide will remain in the subsurface. Similarly old oil fields located, close to power plants prior to abandonment may also be tested if they can serve as host for atmospheric carbon dioxide. Holistic consideration suggests that the cost of doing such a process far outweighs the cost of not doing it. Exposed thick flood basalts cover a large part of onshore India and fractures within basalts can provide locales for injected carbon dioxide.

This can be another area of research for proper site selection. Injected CO_2 can also enhance methane extraction in coal-based methane projects as rocks have a greater affinity towards carbon dioxide compared to methane. They can store carbon dioxide in pores by displacing methane. Enhanced coal-based methane may not be a game changer in India, for the production of coal-based methane is miniscule and injected CO_2 can only displace existing methane.

Sequestration project needs monitoring from time to time to ensure that injected CO_2 does not leak back to the atmosphere, and displaced saline water does not contaminate fresh water. Proper site selection in the subsurface is crucial for the success of the project. Time lapse 3D seismic data along with reservoir pressure and temperature data can help at least qualitatively in monitoring stored carbon dioxide, and a quantitative assessment of the entrapped volume of carbon dioxide is also possible in favourable situation especially in EOR processes. However in India, oil and gas fields are not in proximity to power plants, barring Gujarat and Andhra Pradesh. Saline aquifers are more widely spread and could be a plausible option for geological sequestration of carbon dioxide.

4.2 Geological Storage

Saline aquifers can store much larger volumes of CO_2, due to its abundance. Unlike in EOR schemes, the geology of reservoirs which are habitats of saline aquifers have to be studied to ensure leakage of CO_2 back into the atmosphere is within acceptable norms, i.e. 1% leakage in thousand years. Estimating performance of sealing is complex and data intensive and each oil field could be very different. Basic criteria for selection of sites for sequestration in saline aquifers are as follows:

- Basin Scale Criteria for Storage
- Adequate depth (>1000 m)
- Strong confining seals minimally faulted, fractured or folded
- Adequate volume and permeability for storage
- No significant digenesis.

Although aquifers are widely distributed across India and offers a huge storage potential, including stack storage, implementation of large-scale injection of CO_2 to fill the capacity is complex (McPherson 2001). In low permeability or compartmentalized reservoirs, pore pressure increases with injection which can create geo-mechanical damage, breaching seal. Sustained injection of CO_2 may also incur wide-scale brine displacement out of adjacent sealing layers, depending on the injection history, initial brine composition and hydrologic properties of both aquifers and seals creating another environmental threat posed by contamination of sweet water aquifers by brines, besides leakage of injected CO_2 into the atmosphere. Extensive aquifers with favourable properties like high permeability of rocks, large thickness of reservoir and capacity to drill large number of injected wells, adequately spaced and extensive seals are some of the selection criterion for ideal locales of injected carbon dioxide in saline aquifers. Regular monitoring to ensure quality seal is necessary.

Sleipner field (Goel et al. 2015) in the North Sea in the Norwegian region is one of the widely known examples of sequestration in saline aquifers. Injection commenced in 1996 with CO_2 separated from natural gas and injected into the Utisara sand, a saline aquifer of late Cenozoic age at a depth of 1012 m below sea bed, around 200 m below reservoir top with a storage of over 11 Mt. Time lapse surveys have been carried out with 3D surveys in 1994, 1999, 2001, 2002, 2004, 2006, 2008 etc. The CO_2 plume is seen in seismic as a number of sub-horizontal reflectors of tuned wavelets arising from thin layers of CO_2 trapped beneath thin intra-reservoir mudstone and the reservoir cap rock and growing in time. There is also a velocity pull down in reflectors below the plume. A post-stack stratigraphic inversion of the 1994 and 1996 provided p wave impedance. Prestack inversion of the 1994 and 2006 data sets (after injecting 8.4 Mt) with 50 iterations in the window 750–1400 m provided Shear wave impedance and refined P or body wave impedance. This results when combined with spectral decomposition gave an idea of the thickness of CO_2 layers thus making it possible to make a volumetric estimate of CO_2 in the subsurface.

Carbon Capture and Sequestration demonstration project (Jiao et al. 2011) in Ordos Basin, China, operated by the Shenhua Group, is the only one in Asia, to put the multilayer injection technology into practice. Studying the influence of temperature, injection rate and horizontal boundary effects on CO_2 plume transport in saline formation layers at different depths and thicknesses, focusing on the variations in CO_2 gas saturation and mass fraction of dissolved CO_2 in the formation of brine in the plume's radial 3D field around the injection point, and interlayer communication between the aquifer and its confining beds of relatively lower permeability and simulating flow and pressure configurations in response to small-scale CO_2 injection into multilayer saline aquifers is a requisite. The modelling domain involves a complex multilayer reservoir-cap rock system, comprising of a sequence of sandstone aquifers and sealing units of mudstone and siltstone layers extending from the Permian Shanxi to the Upper Triassic Liujiagou formation systems in the Ordos Basin. Simulation results indicate that CO_2 injected for storage into deep saline aquifers cause a significant pressure perturbation in the geological system that may require a long duration in the post-injection period to establish new pressure equilibrium.

The multilayer simultaneous injection scheme exhibits mutual interference with the intervening sealing layers, especially when the injection layers are very close to each other and the corresponding sealing layers are thin. Injection rate and temperature are the most significant factors for determining the lateral and vertical extent that the CO_2 plume reaches and which phase and amount will exist at a particular time during and after the injection. In general, a large number of factors may influence the CO_2—water fluid flow system considering the complexity in the real geologic sequence and structural configurations. Therefore, optimization of a CO_2 injection scheme still requires pursuance of exhaustive research. Rigorous monitoring of reservoir fluid either through pressure studies in slim hole for thinner reservoirs or time lapse seismic for seismically resolvable reservoirs is a significant approach in recent times. This however will increase the cost of power and calls for political will but surely will be a necessity to protect the blue sky from turning gray permanently.

5 Seismic Monitoring

Acoustic and elastic impedance (Goel et al. 2015) contrast between the overlying and underlying rock strata and the reservoir rock provides the basis for subsurface imaging of the reservoir. While the longitudinal wave (P wave) is sensitive to the pore fluid, the transverse shear wave (S wave) bypasses the pore and therefore, is insensitive to the presence of fluid. Gassman's equation provides a relationship between P wave velocities Vp, S wave velocity Vs, average density of matrix and fluid, porosity and elastic constants of rock matrix and fluid. Fluid substitution assuming constant shear modulus and constant porosity can help in modelling the change in p wave velocity with injected CO_2. Calibration of seismic with well log data, wavelet estimation and generation of a low frequency model are requisite prior to pre-stack seismic inversion which provides Vp and Vs. A cross plot of VP/Vs with injected carbon dioxide volume can be helpful in inferring volume of injected and entrapped carbon dioxide. This also needs to be further cross checked with rock physics, for each case is unique, for besides rock's petro physical properties' interaction of dissolved carbon dioxide with host rock can make a major impact. A baseline 3D survey prior to CO_2 injection, and then with 3D survey repeated periodically along with injected CO_2 and Oil and brine production as the case may be and interpreting changes in Seismic and reservoir temperature and pressure can help in monitoring injected CO_2.

Repetitiveness of seismic acquisition and processing needs to be ensured in the time lapse 3D surveys to attribute changes in seismic data to the injected CO_2. This has to be checked at the non-reservoir zone where CO_2 has not been injected. Differences in Seismic in the reservoir zone, over and above the non-reservoir, if self-consistent with the increasing injected volume can enhance credibility of interpretation. Permanent sensors placed in the ground during the sequestration process helps to maintain consistent receiver parameters across surveys in order to achieve repeatability. While quantification of injected volume may not always be feasible depending upon the physical and chemical reaction of the injected carbon dioxide with the rocks and pore fluid, yet qualitative inference and monitoring will normally be feasible. A leakage if any is relatively simpler to detect in Seismic and is essential. In case the deeper super critical carbon dioxide in liquid state breaches the seal and during its migratory upward path gets entrapped into shallower strata, then since this liquid carbon dioxide will be in gaseous form it will be easier to detect in Seismic. Integration of reservoir simulation studies with seismic time lapse provides the key to successfully inject large volumes of carbon dioxide and ensure that they remain entrapped. All this comes at a cost.

6 Carb Fix Pilot Project in Iceland

An experimental project (Matter 2016) was designed to promote in situ CO_2 mineralization in basaltic rocks for the permanent disposal of anthropogenic CO_2 emissions. Two injection tests have been performed at the Carb Fix injection site near the Hellisheidi geothermal power plant situated about 25 km east of Reykjavik, designed with a 2000 m-deep injection well and eight monitoring wells ranging in depth from 150 to 1300 m. The target CO_2 storage formation is between 400 and 800 m depth and consists of basaltic lavas and hyaloclastites with lateral and vertical intrinsic permeability's of 300 and 1700×10^{-15} m^2, respectively and overlain by low-unit permeability hyaloclastites. The formation water temperature and pH in the injection interval range from 20° to 33 °C and from 8.4 to 9.4, and it is oxygen depleted. CO_2 and H_2S are injected by fully dissolving in water in injection well. To avoid potential degassing, the CO_2 concentration in the injected fluids was kept below its solubility at reservoir conditions. Once dissolved in water, CO_2 is no longer buoyant and it starts to react with the Ca–Mg–Fe–rich reservoir rocks. Fluid samples were collected in the injection well and the monitoring wells. The fate of the injected CO_2 was monitored with a suite of chemical and isotopic tracers carbon-14 (^{14}C) to monitor its transport and reactivity monitoring. The CO_2 and CO_2/H_2S mixtures, fully dissolved in water together with the tracers, were injected into the target storage formation with typical injection rates, being 70 g/s for CO_2 and 1800 g/s for H_2O, respectively with a total injection of 175 tonnes of pure CO_2 from January to March 2012 during phase I. Injection rates during phase II varied between 10 and 50 g/s for CO_2 and 417 and 2082 g/s for H_2O with a total injection of 73 tonnes of a CO_2-H_2S gas mixture in June to August 2012, of which 55 tonnes were CO_2. The results of the study showed that 95% of the injected CO_2 was mineralized through water-CO_2-basalt reactions between the injection and monitoring wells within 2 years. Most of the injected CO_2 was probably mineralized within the porous matrix of the basalt that allows for longer fluid residence times and thus extended reaction time. The fast conversion rate of dissolved CO_2 to calcite minerals in the Carb Fix storage reservoir is most likely the result of several key processes as below

(i) the novel CO_2 injection system that injected water-dissolved CO_2 into the subsurface;
(ii) the relatively rapid dissolution rate of basalt, releasing Ca, Mg and Fe ions required for the CO_2 mineralization;
(iii) the mixing of injected water with alkaline formation waters;
(iv) The dissolution of pre-existing secondary carbonates at the onset of the CO_2 injection, which may have contributed to the neutralization of the injected CO_2-rich water via the reaction.

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \quad (1)$$

Deccan traps were widely deposited during Cretaceous period as flood basalts across vast areas of Peninsular India, and are found in outcrops as well as in subsurface. Older Rajmahal traps were deposited in the eastern part of India. Through seismically opaque and located for from power plant pilot project should be designed to pave the way for a greener India in spite of need to grow coal-based power plants.

7 Conclusions

Carbon dioxide sequestration for enhanced oil recovery has been carried out in USA, Canada and Brazil very successfully. The technology is well known. However the complexity of the process makes each case unique in its own way. Techno commercial feasibility studies including reservoir simulation has to be done pre-injection. Besides sequestration, there are many other methods through which enhanced oil recovery is carried out and thus oil companies have less incentives in trying out sequestration only as a tertiary recovery.

India has to increase its power generation multi-fold. Per capita electricity consumption is a fraction of the world average and with growth this is bound to increase. Most of the power plants are coal based. They generate huge volumes of carbon dioxide and flue gases and many of these power plants are located far away from oil and gas fields. Injection of carbon dioxide into saline aquifer is therefore necessary to protect our environment. Injecting large volumes of carbon dioxide in a time bound manner in saline aquifer without geo-mechanical damage to the host rock, ensuring a permanent storage of carbon dioxide and non-contamination of ground water by the displaced saline water is a major technical challenge. Proper site selection is paramount and this has to be based on reservoir simulation studies. Depleted oil and gas fields whose geology is known and which are in proximity to power plants can be the ideal choice for sequestration with or without production of additional oil. Success as reported in the pilot project at Iceland to trap carbon dioxide in mineralised forms within basalts is a break through. Similar pilot project needs to be undertaken in India. Other area of concern is the additional costs that need to be incurred which the power consumer has to pay. Initiative has to come from the environment sector, for the cost of not doing it far exceeds the cost of doing it. This could be taken up as a multi-disciplinary project with the involvement of Power, Coal, Research Institutes, Oil sector and others under the aegis of Ministry of Environment.

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Chapter 13
Coalbed Methane: Present Status and Scope of Enhanced Recovery Through CO_2 Sequestration in India

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Abstract Enhancing coalbed methane recovery through injection of CO_2 in depleted low pressure coal reservoir is a potential, economic and environmentally suitable solution to reduce greenhouse gas emissions. In India, commercial coalbed methane (CBM) production has been started since 2007 at Raniganj and Sohagpur basins and subsequently to Jharia and Bokaro coalfields. CBM reservoirs are at low pressure, and after some years of production through primary reduction of hydrostatic pressure, rate of recovery declines and harms the well economics. In a secondary drive, the CO_2 or $CO_2 + N_2$ or other mixture of gases can be injected to enhance the methane recovery and to maintain reservoir pressure. Studies conducted so far support stronger affinity of CO_2 to the coal molecule, displacing each methane molecule by 2–3 molecules of CO_2. Coal may adsorb more carbon dioxide than methane and that carbon dioxide is preferentially adsorbed onto the coal structure over methane (with 2:1 ratio). High-pressure methane and CO_2 sorption measurements were carried out for various coal seams in India. On the basis of CO_2 sorption capacity, seam thickness and extension, the suitable sites and their storage capacities estimated to be 4459 Mt for CO_2. It is assumed that this quantity of storage is sufficient to store over 20% of total gas emission from the present power plants over their lifetime. The sites close to the operating thermal power units may be the most appropriate for CO_2 sequestration as the transportation cost of the gas will be minimum. The rate of CO_2 generation and total CO_2 generated within the life span of a thermal power station presuming 20 years more from the date will be helpful for enhanced coalbed methane (ECBM) process in the close vicinity of CBM blocks. It is also required that geologic data and experimentally determined

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mineralization reaction rates and kinetics should be incorporated into geochemical models to predict the permanent storage of CO_2 in unmineable deep coals after ECBM recovery.

Keywords Enhanced coalbed methane · Recovery · CO_2 sequestration · Sorption isotherm · Storage estimates · Unmineable coal seams

Abbreviations

CBM	Coalbed methane
ECBM	Enhanced coalbed methane
ONGC	Oil and Natural Gas Corporation
GEECL	Great Eastern Energy Corporation Ltd
CSIR	Council of Scientific and Industrial Research
CIMFR	Central Institute of Mining and Fuel Research
CDM	Clean Development Mechanism
bcf	Billion cubic feet
IGCC	Integrated Gasification Combined Cycle
PFBC	Pressurized Fluidized Bed Combustion
CSLF	Carbon Sequestration Leadership Forum
IWCCS	International Workshop on Carbon Capture and Storage
DGH	Directorate of Hydrocarbons
HBJ	Hazira Bijaipur Jagdishpur
IPHE	International patnership for hydrogen economy
TCF	Trillion cubic feet
ICOSAR	Indian CO_2 sequestration applied research
VR	Vitrinite reflectance
BCM	Billion cubic meters

1 Introduction

In India, the Coalbed methane (CBM) recovery and utilization on large commercial scale is gaining importance. After few years of primary recovery, the rate of production declines and harms the well economics. At this stage injection of CO_2 into coal beds, enhanced methane recovery helps to tackle the dual challenges of reducing carbon dioxide and improving quality of life through clean energy exploitation (Reichle et al. 1999). There are many technological barriers and different challenges have to be overcome in the initial stages such as land acquisition, complex geologic conditions, drilling in heterogeneous formations, multiple hydrofrac and economic recovery techniques.

Coal seams can hold large amounts of carbon dioxide in comparison to the amounts of methane gas that they contain (Burruss 2003). However, before commercial sequestration projects are undertaken, it is necessary to evaluate the consequences of the geologic sequestration of carbon dioxide. Several efforts have been made in the past to investigate different technical issues related to carbon dioxide sequestration in unmineable coal seams (Bromhal et al. 2003; Mavor et al. 2004; Gorucu et al. 2005; Reeves and Oudinot 2005; Siriwardane et al. 2006). Coal swelling and shrinkage is considered as one of the potential problems during the carbon dioxide sequestration (Reeves and Oudinot 2005; Smith et al. 2005; Kelemen et al. 2006; Mazumder et al. 2006a, b; Pan and Connell 2005). Several laboratory experiments and numerical studies indicate that coal undergoes simultaneous swelling and shrinkage when the carbon dioxide is injected into a coal seam while the methane is produced. The large CO_2 adsorption capacities of coals and the CO_2-induced swelling of coals are two properties that were documented early (Mahajan 1991; Levine 1996). The research priorities for coal seam sequestration are sorption of CO_2 and coal swelling behaviour caused by CO_2 adsorption (Reichle et al. 1999). Studies in these and related areas will help define the CO_2 trapping mechanisms. Amoco has studied the adsorption of nitrogen, methane, carbon dioxide, and their mixtures to provide data for the modelling of gas recovery from coalbed methane reservoirs (Chaback et al. 1996; DeGance et al. 1993). Burlington Resources, the largest producer of coalbed methane, has been injecting CO_2 to enhance methane production since 1996 (Stevens et al. 1998). The experiences gained from enhanced oil and gas recovery of conventional reservoirs can be used for Enhanced Coalbed Methane (ECBM) recovery and also to the long-term disposal of CO_2.

Coal is an especially attractive target for sequestration not only because it can store large quantities of gas, but because CO_2 can be used to enhance recovery of coalbed methane, thereby offsetting the costs associated with sequestration of CO_2 (Byrer and Guthrie 2000; Gentzis 2000; White et al. 2005). It is essential, before finalization of CO_2 disposal sites that under what environmental conditions the sequestered CO_2 would remain stable, a better understanding is needed of the chemistry of the coal-CO_2 and methane displacement. One of the earliest studies of the adsorption of CO_2 on coal used the BET equation to calculate the CO_2 surface areas of anthracites (Walker and Geller 1956). The diffusion of CO_2 through coals of various ranks as an activated process was established not long afterward (Nandi and Walker 1965). Despite the fact that these, and many studies since then, have been performed at low pressure and of tenet low temperature in order to investigate the surface area of the coal (Mahajan 1991), they have provided information which is relevant to today's sequestration projects.

Coalbed methane reservoirs in the lower Gondwana and Tertiary Formations are extremely heterogeneous and this heterogeneity must be considered to screen areas for the application of CO_2 sequestration and ECBM recovery technology. Major screening factors include stratigraphy, geologic structure, geothermic, hydrogeology, coal quality, sorption capacity, technology and infrastructure. Results of this investigation indicate that the potential for CO_2 sequestration and enhanced coalbed methane recovery in the Indian coal bearing basin is substantial and can result in significant reduction of greenhouse gas emissions while increasing natural gas reserves.

2 Coalbed Methane Status in India

CBM has a very bright future in India if proper steps are taken in this direction. Currently, seven CBM blocks have been operated by Oil and Natural Gas Corporation (ONGC), Essar, Reliance and Great Eastern Energy Corporation Ltd. (GEECL) producing methane commercially. India, having the fourth largest proven coal reserves (306 billion tonnes) and being the third largest coal producer in the world, holds significant prospects for commercial recovery of CBM on large scale, it is anticipated that by 2022, CBM may contribute 10–16% of natural gas requirement.

The prognosticated CBM resource based on the Council of Scientific and Industrial Research (CSIR)-Central Institute of Mining and Fuel Research (CIMFR) determined in situ gas content and sorption capacities has been estimated to be around 4.6 TCM by Directorate of Hydrocarbons (DGH). Till now, 32 CBM blocks have been awarded in four rounds of international competitive bidding and on nomination basis. CIMFR has carried out detailed investigation to evaluate the coalbed methane reservoir parameters such as in situ gas content, molecular gas composition, sorption capacity, petrography, coal quality, thickness of coal seams, porosity, permeability and geo-mechanical properties. In situ gas content obtained through the direct method and initial recovery of methane from production wells encourages the large-scale future commercial production in coalfields such as Jharia, Bokaro, Raniganj, North Karanpura and Sohagpur. The CBM production may rise from the current 1.6 million metric standard cubic metres per day (mmscmd) to 10 mmscmd in 2022, reflecting a tremendous growth in CBM production.

India is endowed with bituminous coal of Palaeozoic and Tertiary ages within the CBM window at depths of nearly 200–1500 m. It is emphasized that Gondwana coal rank varies both laterally and vertically and changes from volatile sub-bituminous to bituminous coals (0.62–1.79% Ro). Coals are composed of 60–85% vitrinite, 15–40% inertinite, small amount of liptinite maceral and a trace amount of minerals. Methane adsorption isotherm determined as 13.91–29.54 m^3/t revealed that the maximum sorption capabilities of coals are affected by coal rank, high ash percentage, coal maceral, coal lithotype and especially to the high moisture content. Estimated gas contents range from 0.5 to 22 m^3/t. In combination with the geological information, the data indicated that the tectonic evolution of the basin had important influences on gas accumulation, preservation and escaping. The permeability is between 0.1 and 10 mD and the porosity ranges from 2 to 7%.

In Raniganj South, GEECL is the first commercial producer of CBM gas in India. It is engaged in exploration, development, production, distribution and sale of CBM gas. It currently owns two CBM gas blocks, one in Raniganj (South), West Bengal and other in Mannargudi, Tamil Nadu. The company started producing CBM gas commercially at the Raniganj (South) block in 2007. It has an estimated 2.4 trillion cubic feet (tcf) of original gas reserve in this block, spread over approximately 210 sq km, and produced 88.02 million metric standard cubic meter (mmscm) in 2013 from 157 wells. The company delivers CBM gas to more than 31 industrial customers through its own pipeline network in the Asansol-Durgapur industrial belt, which includes steel plants, steel rolling mills, glass, chemical and food industries. Compared with the other major U.S. CBM basins, GEECL's Raniganj (South) block displays remarkable similarities with the Black-Warrior basin of USA where multiple coal seams with significant gas content and favourable permeability account for high productivity. In Raniganj East, Essar Oil producing around 7,00,000 scm/d of gas. The total proven and probable reserves at Raniganj, evaluated as 113 billion cubic feet (bcf) gross. Nearly 150 wells have been placed on gas production; additional 155 wells have been drilled and are at various stages of the hydrofracking-completion-dewatering cycle for further gas production. In Sohagpur, Reliance Industries Limited (RIL) has done 12 core holes and two test wells in the block. Gas-In-Place of the order of 54.5 billion cubic metres (bcm) has been established. It is quoted that gas-in-place estimates are much more than the initial estimates done by DGH. Two test wells are producing incidental gas, from day one of dewatering, with rate more than 4000 m^3/day. The commercial quantities of CBM gas once produced from Sohagpur block can be consumed for captive power generation. Alternatively, it can be transported to nearby Hazira Bijapur Jagdishpur (HBJ) pipeline, which is at a distance of about 300 km, to reach wider markets through a dedicated pipeline. Usage through CNG is also possible in this area.

3 CO_2 Emissions in India

The top four emitting countries in the world, which together account for almost two-thirds (61%) of the total global CO_2 emissions are China (30%), the United States (15%), the European Union (EU-28) (10%) and India (6.5%). The present per capita annual CO_2 emission in India is estimated as 1.7 t as compared to 4.7 t world average and 17.0 t that of the US (World Bank 2015). By this level, even the planned combustion of coal by 2025 is likely to generate CO_2 just at par to the world average. India as such cannot be treated as the one responsible for emitting disproportionately high CO_2. Per capita CO_2 generation level in India is much below the world average and even with the planned power generation rate, expected to remain within the average numeral. This however does not give an excuse to forget ways and means to control the CO_2 emission in the interest of the global fraternity. Taking the benefits of latest technological innovation, the possible options to keep emission under control in near future are such as (i) use of Integrated Gasification Combined Cycle (IGCC) of Pressurized Fluidized Bed Combustion (PFBC) fuel efficient combustion technology to get more electricity from using less coal and reducing CO_2 emissions, (ii) capturing of methane from the coal beds and converting to CO_2 after using the heat energy and (iii) storage of CO_2 in unmineable coal beds while enhancing the methane recovery from the coal beds.

All the options are being adopted in leading countries and it is in the interest of India to follow suit. A part of CO_2 sequestration expenditure in all the trials is offset by additional methane recovery from the coal beds. India for one could take the advantage and help in minimizing CH_4 concentration in the environment and storage of CO_2 in deep coal beds keeping the financial burden to minimum.

4 Carbon Capture and Storage Activities in India

India is a major coal user and its demand is growing rapidly (IEA 2007). Approximately half of India's current annual CO_2 emissions of over 1300 Mt are from large point sources that are suitable for CO_2 capture. In fact, the 25 largest emitters contributed around 36% of total national CO_2 emissions in 2000; indicating important CCS opportunities (IEA GHG 2012). As a non-Annex I country to the United Nations Climate Change Convention, India has agreed to complete GHG emission inventories but is not required to meet an emissions reduction target. Further, because of the abundance of coal in India, combined with rapidly growing energy demand, the government of India is backing an initiative to develop up to nine Ultra-Mega Power Projects. This will add approximately 36 GW of installed coal-fired capacity in India. If the Clean Development Mechanism (CDM) Executive Board approves a CCS methodology, CCS projects could be certified for carbon trading under the Clean Development Mechanism, offering an important injection of funding that is needed. The Department of Science and Technology, Technology Bhawan in New Delhi launched the Indian CO_2 Sequestration Applied Research (ICOSAR) network in 2007 to facilitate dialogue with stakeholders and to develop a framework for activities and policies studies. CCS research in India includes CO_2-EOR scoping studies that are being carried out in mature oil fields; acid gas from the Hazira processing plant to be injected and reservoir properties (fluids, injection depth) indicate project feasibility. IGCC costs become 63% higher with capture than without capture (Goel 2007, 2008). India has joined a number of international efforts to advance the development and dissemination of CCS technologies. These include participation in the Carbon Sequestration Leadership Forum and the International Partnership for a Hydrogen Economy (IPHE), joining the US on the Government Steering Committee for the US Future Gen project, the US Big Sky CCS partnership, and the Asia Pacific Partnership for Clean Development and Climate. CCS workshops and knowledge sharing events have been organized, including the International Workshop on Carbon Capture and Storage (IWCCS) in 2007 in Hyderabad and the 2006 Carbon Sequestration Leadership Forum (CSLF) meeting in Delhi (Goel 2008). However, India's official position has not favoured the assessment of CO_2 storage potential in India or the implementation of a zero-emissions fossil-fuel power plant given the higher cost and technical uncertainties associated with CCS technologies.

5 Sorption of CO_2 and Methane

Methane adsorption capacity has been found useful for estimating CO_2 sorption capacity in the US coal fields and elsewhere. The required characteristics of the selected coal beds—vitrinite reflectance percentage and proximate analysis are found to be the relevant parameters affecting the gas recovery and subsequently CO_2 sequestration in coal beds. The coal mass has methane in micropores invariably less than the adsorption capacity of the coal. The adsorption capacity of the coal has been studied in the US, Canada, Australia, India and China. It is invariably found to be higher than the resource capacity indicating free surface area on coal molecule. Injection of CO_2 in such coal beds have the option of occupying the void and or occupy the total surface area by even displacing the methane molecules. The studies conducted so far support the later option because of stronger affinity of CO_2 to the coal molecule. It has been found that with the displacement of each methane molecule, 2–3 molecules of CO_2 are accommodated and thus its adsorption reaches closer to near complete (Mendhe et al. 2007).

The adsorption, storage and generation of methane are also known to depend upon the surface area of microporous system, thickness of coal seams/volume of coal and the confining pressure. A few of them have been explored for methane content under deep cover. Methane sorption capacity for Indian coals has been investigated by CIMFR. Based on the research of the last two decades, it has been generally accepted that coal can adsorb more carbon dioxide than methane and that carbon dioxide is preferentially adsorbed onto the coal structure over methane (Greaves et al. 1993; Arri et al. 1992). The 2:1 ratio has been widely reported in the literature (Smith 1999, Byrer and Guthrie 2000; Gentzis 2000; Chikatmarla and Bustin 2003). However, recent studies indicate that this ratio can vary widely from more than 10 in low-rank coals to less than 2 in medium and low volatile bituminous coals (Stanton et al. 2001). Also some laboratory studies indicated that this ratio can be higher at pressures higher than 9.6 MPa (1450 psi), when gaseous CO_2 is changed into supercritical CO_2 (Hall et al. 1994). Understanding controls on CO_2 and CH_4 adsorption in coals is important for the modelling of both CO_2 sequestration and CBM production, yet the science on this subject is still in very early stages.

6 Estimation of in Situ Gas Content in Coal

The CBM recovery prospects in the absence of detailed exploration and study is estimated by empirical approaches like Langmuir adsorption Isotherm and Kim's equation (Kim 1977). The generation volume of thermogenic methane as per Meissner empirical equation is related to volatile matter (dry ash free basis) and rank of coal (Meissner 1984). The approach for estimation of gas in place is even more approximate depending upon the gas content and geometrical parameters like seam thickness, area and density of coal (Mukherjee et al. 1999). The equation of Kim empirical equation is based on adsorption isotherm and chemical composition of coal (Kim 1977). The volume of gas likely to be available is estimated by Direct and Indirect methods followed on coal samples in laboratory condition (Mukherjee et al. 1999).

Step in Direct Method

(a) Measurement of lost gas after the coal sample is cut by drilling bit and received in sealed container on the surface.
(b) Measurement of gas desorbed from the sample.
(c) Measurement of residual gas that remains in the sample after desorption ceases.
(d) Plot of the above quantity may be extrapolated to estimate gas likely to be available from a particular coal bed.

Step in Indirect Method

(e) Adsorption test for maximum quantity of gas a coal sample can hold by generating adsorption isotherm.
(f) Plot the adsorption quantity against pressure till equilibrium.
(g) Decrease the pressure and plot the gas volume against different pressures.
(h) Match the data with Langmuir's adsorption curve to estimate total gas content.

With the confirmed closer affinity of CO_2 to coal, faster rate of adsorption 2:1 and fixing of 2–3 mol in place of one mole of methane, the estimation of CO_2 storage may be treated by direct method of adsorption test for different coals. Given this opportunity, CO_2 adhere to the coal matrix with bond stronger than methane, amount stored is 8–9 times more by weight and volume is near total surface of the coal matrix. Based on methane sorption capacity, CO_2 sorption capacity of coal has been estimated for different Indian coals. The CO_2 sorption capacity, available coal reserve and CO_2 storage potential for different sites based on these assumptions are submitted below.

7 Screening Criteria for ECBM Using CO_2

The geologic factors determining the distribution and reducibility of coalbed methane resources are essentially the same as those determining carbon sequestration potential and include stratigraphy, structure, hydrogeology and sorption capacity. Technology and infrastructure must also be considered when screening areas for the demonstration and implementation of carbon sequestration technology. Emerging technologies to be considered include CO_2 separators for flue gas and enhanced gas recovery technology. A vital goal of sequestration is to deliver CO_2 at low enough cost so that coalbed methane remains economically viable on the open market. Once enhanced coalbed methane recovery is established, the groundwork can be laid for more intensive carbon sequestration efforts independent of the natural gas industry. Carbon sequestration further has potential to improve safety in underground coal mines and abandoned mines can play a role in the separation of CO_2 from flue gas. Infrastructure plays a critical role in the ways that carbon sequestration programs can proceed. Although a lack of infrastructure in many undeveloped basins may limit the applicability of carbon sequestration technology, a high degree of flexibility also exists. For example, flooding coal with CO_2 has potential for use as a primary production procedure that will eliminate concerns associated with water disposal and foster unprecedented recovery of the coalbed methane resource. Following are the major screening criteria for taking up of ECBM projects:

i. In situ gas content of coal seams
ii. Sorption capacity of methane and CO_2
iii. Porosity and permeability evolution due to shrinkage and swelling of coal
iv. Depth of reservoir and sequence stratigraphy
v. Thickness of reservoir
vi. Geological structure
vii. Hydrogeology
viii. Coal Quality
ix. Leakage and mineralization
x. A coal seam has sufficient reserve of CBM
xi. Minimum 1.35 m^3 of gas per tonne of coal is economical for ECBM
xii. Coal bed methane exists in areas where coal bed is buried deep and maintains sufficient water pressure.

Understanding controls on CO_2 and CH_4 adsorption in coals is important for the modelling of both CO_2 sequestration and ECBM production.

8 CO_2 Storage Potentiality in Coal Beds of India

Estimates for the geological storage potential in India are in the range of 400–500 Gt of CO_2, including on-shore and off-shore deep saline formations (300–400 Gt), basalt formation traps (200–400 Gt), unmineable coal seams (5 Gt) and depleted oil and gas reservoirs (5–10 Gt) (Singh et al. 2006). It should be noted that none of the fields that contribute to this value have the ability to store more than 100 Mt. CO_2 storage in deep coal seams is still in the demonstration phase (IEA GHG 2012). Indian coalbed are classified into grey concealed and unmineable based on its depth of occurrence and grade characteristics.

Coal resource distribution of Indian Territory is of Permo-Carboniferous Period in Lower Gondwana sediment's of Barakar and Raniganj formation of Damuda Group (Coal India 1994). Nearly, 14,000 sq km of the same is fairly well explored for coal resources while a large portion is buried deep under sediments of Jurassic to Pleistocene age and recent alluvium (Coal India 1994). The beds even in explored basins are thrown deep by major intra-basinal faults while the beds in some areas are concealed under basalt and inter-trapean formation or thick alluvium. The concealed beds are traced up to 3500 m depth cover. Any coal bed below 2000 m depth cover is not taken as a resource for any purpose including methane recovery and CO_2 sequestration.

8.1 Estimation of Unmineable Coal Beds

The mining limit is decided with due consideration to quality, fuel value, market demand, market price, basin location and abundance of coal. The limit as such varies for different grades of coal and also location of the coalfields. There is no decided guideline for making futuristic extrapolation for mining limit but in the light of past experience and future projection of global technological input. In depth, coal resource analysis of Indian territory as per quality, depth wise distribution and status of exploration has supported in identification of suitable sites for CO_2 sequestration. The resources reported by GSI (2015), and other agencies have been grouped as mineable and unmineable on the basis of the following factors:

(i) Exploration limit of coal has been to 1200 m depth cover.
(ii) Coking and superior grade non-coking up to the explored limit has been classed as mineable.
(iii) Inferior grade non-coking coal (Grade E-G) below 600 m depth cover in.
(iv) Damodar and Mahanadi Valleys have been taken as within mineable limit.
(v) Mineable limit for inferior grade non-coking coal of Godavari and Wardha Valleys have been taken as 800 m due to premium pricing structure.

The coal beds of Singrauli, Mand Raigarh, Talcher and Godavari valley come under the category where the coal reserve is available below the mining limit. With a view to capping injected CO_2 in the coal beds, minimum 100 m thick top formation is proposed to be left between the working horizon and non-mining zone. The vitrinite percentage of these sites is low in the range of 40–60%, vitrinite reflectance (VRo%) within 0.4–0.6% and ash within 15–45%, average 35%. The seams according to these properties are sub-bituminous in rank with poor cleat frequency and aperture. The coal reserve, methane reserve and CO_2 storage capacity for these sites is summarized in Table 1.

8.2 Estimation of Grey Area Coal Beds

The extension of coal beds below 1200 m depth cover in coking and superior grade non-coking coal have not been explored even though the continuity of the coal beds was well indicated within the lineament. The coal beds of such zones beyond

Table 1 Unmineable area coal reserve and CO_2 storage capacity

Coalfield	Estimated adsorption capacity of CO_2 (m^3/t)	Coal reserve (Mt)	CO_2 storage capacity (Bm^3)	CO_2 storage capacity (Mt)	CO_2 storage capacity (90%) (Mt)
Singrauli	Average 20.0	37.0	0.74	1.46	1.32
Mand Raigarh	Range 16.0–23.0 average 19.0	79.0	1.50	2.97	2.67
Talcher	Range 17.2–24.8 average 20.4	1017.0	20.80	41.18	37.06
Godavari	Range 16.8–22.2 average 19.2	1976.0	38.02	75.28	67.75

mineable limit have been classed as Grey Area reserve. These reserves in case of East Bokaro, South Karanpura, Jharia and Raniganj and Sohagpur are below 1200 m depth cover while in case of inferior grade non-coking the limit is 600 m for Son Mahanadi Valley and 800 m for Wardha Godavari Valley coal fields. The coal and CBM, recoverable CBM and CO_2 storage capacity for these areas is summarized in Table 2.

The methane reserve in these locations is within 3.15–11 Bm^3 in 76–450 sq km area. Cumulative seam thickness is very high within 15–120 m and average gas content; within 2.4–7.6 m^3/t of coal. Some of the seams of Damodar valley coal basins have gas concentration above 19 m3/t of coal. Total CO_2 sequestration even with 60% methane recovery is estimated over 114 BCM or Mt. approximately.

8.3 *Estimation of Concealed Coal Beds*

The coal beds not covered in resource estimation exercise because of the basalt trap or thick alluvium beds have been classed as concealed coal beds. Invariably such beds come under chance discovery during oil and natural gas exploration or drilling for some special missions. The bottom most coal bearing Barakar formation in such operations has been located within 300 m to 3 km depth cover over Nagaland to Cambay Basin Gujarat. For the CO_2 sequestration or even ECBM recovery, the beds below 2000 m have not been included in concealed potential sites. In case such sites are indicated roughly and the boundary and lithology is not defined, they are also excluded from the present exercise for the time being. The representative gas content coal rank and CO_2 storage potential for these fields are based on information available for the nearest coal bed of the lineament or from different sources. These values are summarized in Table 3.

The potential CO_2 storage capacity for all the three classes is estimated in the light of general findings of laboratory and field trials of the USA, Canada, Australia and the latest of Poland. As each site is special with individual characteristic, the general findings of the previous studies have been supplemented by the information

Table 2 Grey area coal reserve and CO_2 storage capacity

Coalfield	Estimated CO_2 adsorption capacity (m^3/t)	Cumulative coal seam thickness (m)	Block area (km^2)	Coal reserve (Bt)	CO_2 storage capacity (Bm^3)	CO_2 storage capacity (Mt)	CO_2 storage capacity (90%) (Mt)
South Karanpura	Range 19.5–28.0 average 24.5	73.0	76.0	0.75	18.35	36.33	21.80
East Bokaro	Range 22.3–33.5 average 28.1	100.0	113.0	1.53	42.90	84.94	76.45
Jharia	Range 22.0–56.0 average 34.5	40.0	193.0	1.04	35.96	71.20	64.08
Raniganj	Range 20.8–29.0 average 24.0	30.0	240.0	0.97	23.33	46.19	41.57
Sohagpur	Range 18.9–26.4 average 22.6	15.0	450.0	0.91	20.59	40.76	36.69
Talcher	Range 17.2–24.8 average 20.4	120.0	149.0	2.41	49.24	97.49	87.75

Table 3 Concealed area coal reserve and CO_2 storage capacity

Coalfield	Estimated adsorption capacity of CO_2 (m^3/t)	Cumulative thickness of the coal seams (m)	Area of the block (km^2)	Coal reserve (Bt)	CO_2 storage capacity (Bm^3)	CO_2 storage capacity (Mt)	CO_2 storage capacity (90%) (Mt)
Cambay basin	Range 13.8–19.6 average 16.7	102.0	6900	63.0	1057.81	2094.45	1885.02
Barmer Sanchor basin	Range 128–18.4 average 15.6	100.0	6700	60.0	936.00	1853.28	1667.95
West Bengal Gangetic plain	Range 16.4–23.2 average 18.3	–	–	7.2	131.76	260.88	234.80
Birbhum Coalfield	Range 17.2–24.8 average 20.2	100.0	312.0	4.2	85.08	168.46	151.61
Domra Panagarh	Range 18.6–25.8 average 21.8	48.0	116.0	0.751	16.39	32.45	29.20
Wardha Valley extension	Range 15.7–22.8 average 17.8	13.0	212.0	0.37	6.62	13.11	11.80
Kamptee extension	Range 7.2–9.2 average 8.1	14.0	300	0.57	9.81	19.42	17.48

available about the Indian sites for the methane recovery and storage potentials of CO_2. In the absence of definite information about the parameters like permeability and gas concentration, etc. lower side values have been accepted in empirical calculations.

9 CO_2 Storage Estimates for Indian Coal Seams Through ECBM

Stimulation of methane desorption from the coal beds is planned in a way that it remained stored safely forever. As per the studies conducted in the US, Australia and Canada, CO_2 injection enhances desorption of methane and in place of each methane molecule, three CO_2 molecules are adsorbed on the coal surface. The affinity of the CO_2 with the coal is stronger than the methane and unless the coal mass is disturbed physically it remains stored with a little chemical reaction and transformation. The coal beds subjected to CO_2 injection for enhanced methane recovery should be unmineable and a cap of impervious rock should be maintained to retain the CO_2 for years to come. The CO_2 storage capacity of the identified unmineable, grey area and concealed coal beds is summarized in Table 4.

Table 4 CO_2 storage capacity in candidate sites

Coalfield	CO_2 storage potential in Mt with 90% saturation level			Total (Mt)	Not considered
	Unmineable beds	Grey areas	Concealed areas		
East Bokaro	×	84.94	×	85	
South Karanpura	×	36.33	×	36	
Jharia	×	71.20	×	71	
Raniganj	×	41.57	×	42	
Singrauli	1.32	×	×	1	Insignificant
Sohagpur	×	36.70	×	37	
Mand Raigarh	2.67	×	×	3	Insignificant
Talcher	37.06	87.75	×	118	
Godavari-Ramgundam	67.75	×	?	68	
Cambay basin	×	×	1885.02	1885	
Barmer Sanchor basin	×	×	1667.95	1668	
W Bengal Gangetic basin	×	×	234.80	235	
Birbhum	×	×	151.61	152	
Domra Panagarh	×	×	29.20	29	
Wardha	×	×	11.80	12	Insignificant
Kamptee Coalfield	×	×	17.48	17	Insignificant
Total				4459	4426

The gas resources of the above coalfields as estimated are based on presumption that the saturation level of the coal mass will be nearly 90% during the lifetime of the bore wells, with recovery of methane as per best practice. The storage capacity of some of the candidates are very insignificant particularly those of Wardha Kamptee extensions and unless the limit is precisely delineated, may not be of any use. Similarly, the storage potentials of unmineable beds of Mand Raigarh and Singrauli are very insignificant and even if ignored may not materially change the situation. Delineation of concealed coal basins not yet well defined may make difference in CO_2 storage capacity in future. The Barmer Sanchor basin finding is a clear example of the latest finding of which has improved the CO_2 storage potential. The next target should be North Rajmahal Purnea basin with large point source of CO_2 generation in close vicinity.

10 Assessment of Priority Sites for CO_2 Storage

The identified sites are estimated to have 4459 Mt CO_2 storage potential, sufficient to store over 20% of total gas emission from the present power plants over their lifetime. The power station location of India is however distributed in each state, including the farthest in Punjab and Kerala. In fact prior to 1970, the location of the thermal power stations had nothing to do with the mine site. It is only after 1970, when the power grade coal was exclusively earmarked for the thermal power stations and restriction for transporting high ash coal to remote area was realized the power centre like Shakti nagar in Singrauli, Ralmahal, Talcher, Korba and Ramgundam came into existence. Even now, the power centres are being planned in close vicinity of basins with abundance of inferior grade non-coking coal. In other coalfields, the old designed thermal power units are distributed in Bokaro, Karanpura, Raniganj, Kamptee coalfield and Rewa coalfield.

The sites close to the operating thermal power units may be the most appropriate for CO_2 sequestration as the transportation cost of the gas will be minimum and the pollution level of CO_2 is alarming. The list of such sites and approximate CO_2 generation is summarized in Table 5.

The CO_2 generation in a well-designed thermal power plant of 2000 MW should be around 25,000 t per day but in most of the above units, the estimated emission level is comparatively high. The combustion of inferior grade coal in old-fashioned plants is the main reason for this abnormal pollution rate. This shows the need for advance combustion technology transfer, renovation and management of the existing units. The rate of CO_2 generation and total $CO_{2,}$ generated within the lifespan of a thermal power station; presuming 20 years or more from the date, the storage capacity compatibility for the nearest sites is summarized in Table 6. The sites with storage capacity below 12 Mt have been ignored because of their insignificant size.

The storage capacity of the nearby candidate, daily CO_2 generation and total gas likely to be generated during the lifetime of the power station with the present

Table 5 Power generation sources, and potential CO_2 storage sites

Nearest storage candidate	Power station	Installed capacity (MW/day)	Coal consumption (kg/KWH)	Million KWH per day	Coal combustion (t/day)	CO_2 generation (t/day)
Cambay	Gandhi nagar	330	0.60	?	2500	9200
Barmer Sanchor	Suratgarh	500	0.60	?	4000	14,600
Godavari	Kothagudam	1170	1.08	22.39	24,200	79,900
	Ramgundam	63	0.73	1.45	1060	3900
	Ramgundam STPS	2100	0.63	50.65	31,900	117,000
Total						200,800
East Bokaro	Bokaro A&B	805	0.80	5.70	4560	16,700
South Karanpura	Patratu	770	0.96	5.23	5000	18,300
	Tenughat	420	0.87	4.8	4200	15,400
Total						43,600
Raniganj	Mejia	630	0.70	9.9	6900	22,000
Sohagpur	Amarkantak	290	0.75		2175	8000
Birbhum	Bakareshwar	630	0.77	9.2	7100	26,000
Domra Panagarh	Durgapur-DVC	350	0.62	7.2	4500	16,500
	Durgapur-DPL	390	0.74	4.39	3250	11,900
Total						28,400
West Bengal basin	Kolaghat	1260	0.73	29.0	21,200	77,700
Jharia	Chandrapura	750	0.79	3.39	2700	9900
	Santaldih	480	0.60	3.6	2200	8000
Total						17,900
Rajmahal	Kahalgaon	840	0.84	17.7	14,900	51,000

(continued)

Table 5 (continued)

Nearest storage candidate	Power station	Installed capacity (MW/day)	Coal consumption (kg/KWH)	Million KWH per day	Coal combustion (t/day)	CO_2 generation (t/day)
	Farakka	1600	0.83	34.95	29,000	106,000
Total						157,000
Talcher	Talcher-NTPC	460	1.01	9.4	9500	34,800
	Talcher-STPS	1000	0.75	11.60	8700	31,900
Total						66,700

Table 6 CO_2 storage capacity and point source gas generation in close vicinity

Candidate	CO_2 storage capacity (Mt)	Nearest Point Source CO_2 generation		Mt in life time (20 years)
		t/day	Mt/year	
Cambay	1885	9200	3.36	67
Barmer Sanchor	1668	14,600	5.33	107
Godavari	68	200,800	73.29	1465
East Bokaro	85	16,700	6.10	122
S Karanpura	36	43,600	15.91	318
Birbhum	152	26,000	9.49	190
Domra Panagarh	29	28,400	10.36	207
West Bengal basin	235	103,700	37.85	757
Jharia	71	17,900	6.53	131
Talcher	118	66,700	24.35	487
Sohagpur	37	2175	0.79	16
Raniganj	42	6900	2.51	50

consumption rate of coal shows that the coal beds does not offer very promising sites for even the point emission sources like Shakti Nagar Singrauli, Rajmahal, Korba and Ramgundam. The storage potential howsoever small may help in minimizing the GHG pollution level and should be targeted along with ECBM recovery.

11 Impact Analysis of ECBM Over Regime

CO_2 can be injected into coal seams through ECBM process, the basic requirement for this are such seams with high porosity that can adsorb CO_2 overlaid by impervious fault free caprock that prevents migration of the stored CO_2 upwards or sideways. Coal seams contain methane which can be drilled for and pumped out, and CO_2 injected into the seam. CO_2 adheres to the surface of the coal twice as much as CH_4. This procedure increases production while locking the CO_2 into the coal bed. Several careful studies should, however be made before this option is implemented as follows:

i. Assessment of the efficacy of the injection process and ensuring the safe containment of CO_2. This requires the tracking of the CO_2 migration and to monitor the integrity of the reservoir.
ii. Impact of injection of fluids on the geophysical properties of the CBM reservoir and the change of geochemical properties over infinite time scales should be examined.

iii. Use of suitable geophysical strategies for depth and time frame for monitoring of migration, leakages and seepage issues.
iv. Laboratory studies on changes that take place in physical and hydro geological properties in response to varying saturation pressure, temperature and gas injection states under simulated conditions.
v. Monitoring/verification involving surface/well logging studies using seismic, electrical and electromagnetic techniques. The studies include fluid dynamic studies to monitor the plume location and migration.

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Chapter 14
A Low-Carbon Growth Strategy for India: Synergies from Oxy-Combustion, Carbon Capture, and ECBM

Thomas Weber

Abstract In spite of aggressive development of renewable energy alternatives, the continued use of fossil fuels will remain essential to national economic development for India and other emerging economies. India is ideally positioned to provide a practical demonstration of a suite of technologies that allows the continued use of indigenous resources while substantially limiting conventional and greenhouse gas pollutants. This suite of technologies employs oxy-combustion-based carbon capture systems fitted to a coal-fired power plant coupled with the injection of by-product gases for enhanced coalbed methane recovery. India has coal resources that currently provide an attractive domestic source of methane through conventional coalbed methane recovery techniques. Recent research concludes that enhanced recovery techniques using CO_2 and N_2 injection can provide substantial additional methane production. Highly concentrated anthropogenic CO_2 is produced by carbon capture technologies based on oxy-combustion, while supplemental N_2 can be available from the associated oxygen plant. Selling the CO_2 and N_2 that is produced, helps to offset the additional costs of air separation and CO_2 compression and transportation. The CO_2 thus utilized remains permanently stored in the coalbed, reducing net atmospheric emissions of this problematic greenhouse gas. The Jupiter Oxygen integrated oxy-combustion technology is uniquely suited to reduce costs associated with conventional pollutant removal and carbon capture. Combined with enhanced coalbed methane recovery, it offers a pathway to advance the national development agendas of coal dependent countries.

Keywords CO_2 capture · Oxy-combustion · Coalbed methane recovery · Carbon capture demonstration · Integrated pollution control · Greenhouse gas mitigation · Low-carbon growth

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Abbreviations

GHG	Greenhouse gases
CCS	Carbon capture and sequestration (storage)
CCUS	Carbon capture, utilization, and storage
CBM	Coalbed methane
ECBM	Enhanced coalbed methane
ARI	Advanced Resources International, Incorporated
IPR™	Integrated pollutant removal™
F	Fahrenheit
TCF	Trillion cubic feet
TCM	Trillion cubic meters
JOC	Jupiter Oxygen Corporation
EOR	Enhanced oil recovery
LCOE	Levelized cost of electricity
USGS	US Geological Survey

1 Background

The United Nations projects an increase in global population of two billion by 2050, mostly in Africa and Asia. The International Energy Agency (IEA) in their central scenario, called the New Policies Scenario, projects that roughly three quarters of primary energy use will still come from fossil fuels in 2040, (IEA 2015a). According to the World Energy Outlook 2015 (IEA 2015a), the largest single-country share of the growth in fossil fuel use accrues to India, which accounts for 25% of the total growth. In the process, India is projected to become the world's second largest coal producer and its largest coal importer, (IEA 2015b; EIA 2016).

India's Intended Nationally Determined Contribution as presented at the United Nations Climate Change conference in Paris (COP 21) reaches out for international collaboration on clean coal (Government of India 2015): "In its pursuit of low-carbon growth, India would be focusing on technologies that need to be moved from lab to field and those that require targeted global research along with those that are still in the realm of imagination. One of the important areas of global collaborative research should be clean coal and fossil fuel, energy management and storage systems for renewable energy. Given the current stage of dependence of many economies on coal, such an effort is an urgent necessity."

The historical legacy and continuing release of greenhouse gases by industrialized countries, combined with increasing emissions from combustion of coal and other fossil fuels in developing countries, will push atmospheric concentrations of carbon dioxide (CO_2) and other GHGs to dangerous levels, putting the planet on a warming trajectory that will likely exceed 2 °C above pre-industrial levels. Fortunately, a new set of cleaner fossil energy technologies has emerged to act as a bridge from conventional fossil fuels to abundant, clean, and sustainable forms of energy. Notable among these is carbon capture, utilization, and storage (CCUS), which offsets some of the inherent costs of carbon capture and storage through the benefits of utilization of the CO_2. Among the utilization options practical on a large scale is enhanced coalbed methane recovery (ECBM), which can produce methane from unmineable coal seams, thus reducing net GHG emissions by providing a lower carbon alternative to coal. At the same time that methane is collected from the coal seams, CO_2 is adsorbed for long-term geologic storage, reducing the carbon footprint of the coal or other fossil fuel used for power generation. The use of oxy-combustion at the power plant creates an advantage, i.e., that CO_2 is highly concentrated in the exhaust gas, enabling cost-effective carbon capture. In addition, there is another important synergy between oxy-combustion and ECBM. The nitrogen produced as a by-product of air separation can be used to supplement the CO_2 as an injectable gas for ECBM. Finally, the use of oxy-combustion allows for cost-effective capture of non-GHG pollutants.

As a pioneer in oxy-combustion technology, Jupiter Oxygen Corporation (JOC) developed, demonstrated, and patented the high-flame temperature approach, which leads to efficiency gains in the boiler. These gains have been demonstrated at Jupiter Oxygen's Hammond test facility (Schoenfield et al. 2012). Jupiter Oxygen's vision is that cleaner fossil energy technologies and strategies can help facilitate the deployment of intermittent renewable energy technologies at a significant scale, while minimizing the negative environmental impacts of conventional fossil energy use. As depicted in Fig. 1, this approach is an ongoing cycle where improved technology can meet increasing energy demands while addressing environmental concerns. The demonstration projects envisioned in this chapter would provide a significant contribution to a continuing cycle of improvements in clean energy sourcing.

Carbon capture technologies for coal-fired power plants are associated with the relatively high cost of the carbon capture process. The 2015 IEA report on "Projected Costs of Generating Electricity" states that the levelized cost of electricity (LCOE) from coal-fired generation is expected to increase by 30–70% due to the addition of CO_2 capture using currently available capture technologies. The report further states that by 2030, this cost mark-up could decline through learning effects to a range of 25–40%, assuming a deployment level of around 100 GW for coal-fired CCS plants (IEA and NEA 2015).

Fig. 1 Low-carbon growth through clean fossil energy technology developments

The key to successfully introducing carbon capture technologies in India will be achieving significant cost reduction. That can be realized through utilization of CO_2 and other by-products (including latent heat recovery, water recycling, ash reuse, and nitrogen) from integrated carbon capture systems.

This chapter presents an assessment of the CO_2 utilization potential for India and identifies synergies with integrated carbon capture systems, in order to find a path forward for clean coal technology implementation.

2 Technologies

2.1 Oxy-Combustion

The original motive for exploring oxy-combustion at power plants was the need for a CO_2 source for enhanced oil recovery (Santos and Haines 2005). That early research, which was performed in the 1980s, relied on the recirculation of flue gas to the burners to mimic the gas flow and heat transfer of existing air-fired boilers. Interest has grown considerably since greenhouse concerns provided a new motive, i.e., CO_2 capture and sequestration (CCS) including CO_2 capture, utilization and storage (CCUS).

Unlike other power plant oxy-combustion systems that have flame temperatures about the same as that for air firing, Jupiter Oxygen technology achieves a high-flame temperature by having mainly oxygen in the combustion process. The high temperature flame results in improved radiant heat transfer. This is an especially promising avenue of development for existing and new-build power plants. In this system, flue gas is recycled through the burner only to the extent necessary to feed pulverized coal. Any additional recycle to balance heat exchange is introduced away from the flame, maintaining flame temperature and stability. Jupiter Oxygen's high-flame temperature oxy-combustion technology and patented capture system [co-developed with the U.S. Department of Energy's National Energy Technology Laboratory from its Integrated Pollutant Removal system (IPR™)] offer fuel efficiency gains in the boiler, 95–100% CO_2 capture, air pollutant control (SO_x, NO_x, particulate matter and mercury), latent heat recovery for additional efficiency, as well as process water reuse. This system is depicted in Fig. 2.

A high-flame temperature oxy-combustion test facility consisting of a 15 MW thermal test boiler facility and slipstream capture system was constructed in Indiana, USA. The test facility was operated on natural gas and coal fuels. Parametric studies were performed to determine the optimal performance conditions and to generate the necessary technical data required to demonstrate the technologies are viable technically and economically for commercial demonstration project scale-up. Flame temperatures in excess of 4900 °F (2700 °C) were achieved with high-flame temperature oxy-natural gas combustion, depending on whether additional recirculated flue gases are added to balance the heat transfer. The project

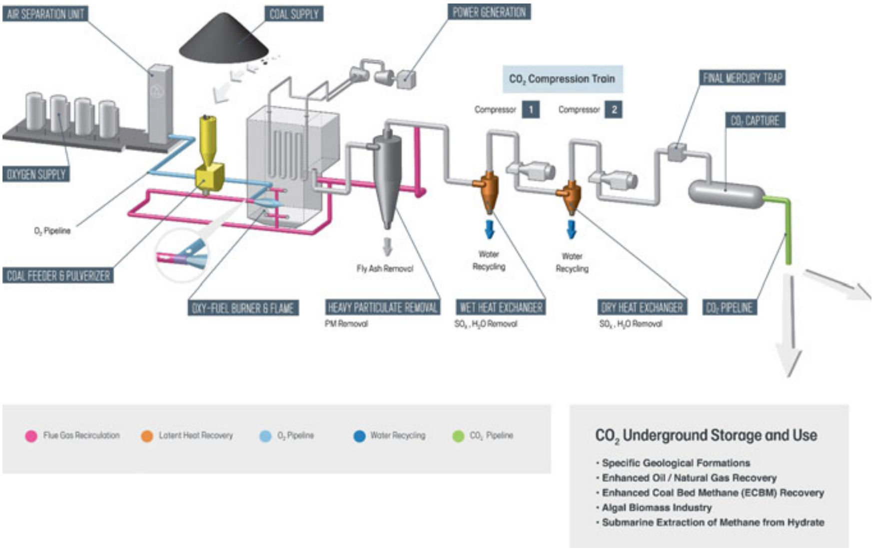

Fig. 2 JOC carbon capture technology (developed in conjunction with NETL)

demonstrated feasibility and effectiveness of the high-flame temperature oxy-combustion process with carbon capture for CCS and CCUS. With these technologies total parasitic power requirements for both oxygen production and carbon capture currently are in the range of 20% of the gross power output. It was concluded that the high-flame temperature oxy-combustion process is ready for commencement of a demonstration project (Schoenfield et al. 2012).

This approach could allow coal-fired power plants today to clean up their CO_2 and other emissions at reasonable cost. Of course, technical and economic feasibility studies will be needed to assess the economic viability of each individual project.

2.2 *Coalbed Methane Recovery*

Coal seams often contain gases such as methane, held in pores on the surface of the coal and in fractures in the seams. Conventional coalbed methane (CBM) extraction is achieved by dewatering and reducing the pressure in the coal seam, so that adsorbed methane is released from the porous surfaces of the coal deposit. The CO_2 moves through the coal seam along its natural fractures (the cleat system), and from there diffuses to the coal micropores where it is preferentially adsorbed.

In coal and shale settings, CO_2 has a higher affinity to become adsorbed onto the reservoir rock surfaces than the methane that is naturally found within them. Upon injection, the CO_2 displaces methane from some of the adsorption sites. The ratio of

CO_2 to methane varies from basin to basin, but has been linked to the maturity of the organic matter in the coal.

In 2009, Advanced Resources International (ARI) estimated that India held 70–90 trillion cubic feet (TCF), i.e., 2.0–2.6 trillion cubic meters (TCM), of CBM resources in place, of which approximately 20 TCF (0.57 TCM) is recoverable (Kuuskraa and Stevens 2009). An additional 15–18 TCF (0.42–0.50 TCM) are potentially recoverable with ECBM.

More recently, the Indian Ministry of Petroleum partnered with the U.S. Geological Survey (USGS) and Oil and Natural Gas Corporation Limited (ONGC) of India to conduct a resource assessment. They estimated that 9–92 TCF (0.25–2.6 TCM) of potential CBM resources exist in India, both onshore and offshore (Ministry of Petroleum and Gas 2016). According to Directorate General of Hydrocarbons (DGH), India the potential CBM resources in India amount to 162 TCF (4.6 TCM), (DGH 2009).

2.3 Enhanced Coalbed Methane

Conventional CBM extraction may leave up to 50% of the methane in the seam after production operations have been completed. Coal deposits have long been regarded as a potential CO_2 storage option, particularly in association with ECBM

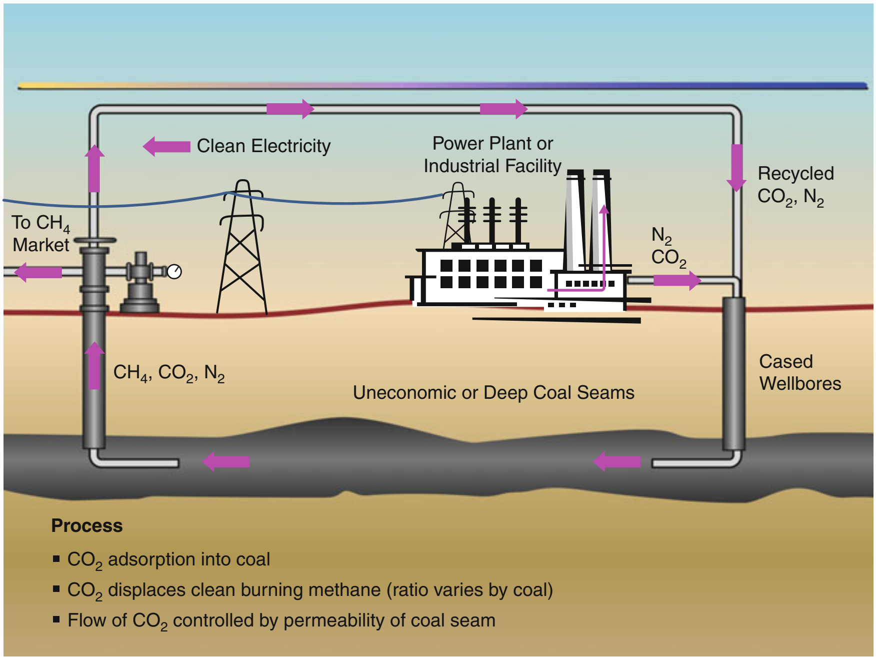

Fig. 3 Depiction of ECBM application

production. The process of ECBM and storage of CO_2 in deep coal seams, as depicted in the schematic of Fig. 3, involves capturing the CO_2 from a flue gas stream, compressing it to high pressures for transport to an injection site, followed by injection into the coal seam.

2.4 *Integration and Synergies*

The Intergovernmental Panel on Climate Change in its Fifth Assessment Report concludes that most climate mitigation scenarios that aim at limiting temperature change to 2 °C rely on the availability and widespread deployment of Carbon Capture and Storage (CCS) technologies in the power and many industrial sectors, including bio-energy with CCS. Furthermore, the International Energy Agency (OECD/IEA 2013) finds that if CCS is removed from the list of options in the energy sector, the capital investment needed to meet the same emissions constraint is increased by 40%. According to the IEA analysis, 70% of all CCS in 2050 will need to be in non-OECD countries, where energy demand is growing and fossil fuels remain the primary domestic energy resources. Enhanced Coalbed Methane Recovery can be used to access domestic resources of natural gas in developing countries that have large resources of coal while simultaneously achieving CCS.

The JOC technology for CCUS is uniquely positioned to offer a pathway to advance the national development agendas of countries like India, China, and Indonesia, while aligning their needs with international efforts to protect the global environment and reduce the risks of rapid climate change. The utilization of CO_2 and other by-products (including latent heat recovery, water recycling, ash reuse, and nitrogen) from integrated carbon capture systems retrofitted to existing pulverized coal-fired boilers can significantly offset parasitic power costs, associated with the carbon capture process, and thus improve overall economics.

Significantly, opportunities may exist for mixing N_2 into the injection stream to improve gas recovery from ECBM. The optimal mix of N_2 and CO_2 has been found to depend strongly on the coal rank, with higher rank coals benefiting from higher N_2 content. A Jupiter Oxygen-sponsored study (ARI 2015) has recommended an effective N_2–CO_2 mix for specific seams. These recommendations are summarized in Table 1.

Table 1 Effective N_2–CO_2 mix for various coal types

Coal type	Effective N_2–CO_2 mix
Low-rank sub-bituminous	20% N_2, 80% CO_2
Medium-volatile bituminous	30% N_2, 70% CO_2
Anthracite	45% N_2, 55% CO_2

ARI (2015)

3 The Opportunity

3.1 ECBM Potential in India

India's large coal reserves and experience in developing and producing conventional coalbed methane (CBM) provide substantial opportunity for enhanced coalbed methane (ECBM) production using CO_2 (and possibly N_2). Very little ECBM activity has been pursued to date. Approximately 20% of the gases in place are potentially recoverable with ECBM, with storage capacity of billions of tons of CO_2. The previously referenced ARI report, "Screening-Level Assessment of CO_2 Enhanced Oil Recovery and Enhanced Coalbed Methane Opportunities in India" (ARI 2015), focused on identifying potential early opportunities for large scale, economically viable utilization of CO_2 for ECBM and CO_2-EOR in India. To accomplish this, three streams of activity have been undertaken:

I. Review past experience with coalbed methane (CBM), and CO_2-EOR projects in India.
II. Estimate ECBM and CO_2-EOR potential and associated CO_2 requirements in areas where their application appears potentially feasible and cost-effective.
III. Match areas appearing to be amenable to ECBM or CO_2-EOR with areas of high levels of CO_2 emissions from power plants to identify possible early "win-win" opportunity.

Key findings of the ARI report include the following:

a. The Gondwana sediments of eastern India host the bulk of India's coal reserves and all of the current CBM producing fields.
b. In total, 824 million metric tons of CO_2 storage capacity could exist in the unmineable coal seams in these current CBM producing areas.
c. Depending on the geographic location and the local geologic characteristics of the target coal seam, all of the areas with current CBM activities underway could contain good prospects for a commercially viable CO_2 storage-ECBM project.

Almost 2.6 TCF (0.073 TCM) is estimated to be technically recoverable from the application of conventional primary CBM technology, and another 1.9 TCF (0.055 TCM) could be recoverable from the application of ECBM in those current CBM producing fields.

4 "Win–Win" Opportunities for CCUS and ECBM Projects

Possible "win–win" opportunities were identified by matching areas appearing to be amenable to ECBM with areas of high levels of CO_2 emissions from power plants. With this in mind, an effort was also made to identify and characterize possible project partners for a demonstration project in India. Thus, the various areas with ongoing or planned CBM production were ranked by the following factors, in relative importance:

- The availability of existing CBM infrastructure to be utilized to allow cost-effective ECBM
- Proximity to existing CO_2 sources
- Willingness, need, and ability of existing CBM producers to pursue an ECBM pilot
- Characteristics for viable ECBM, including areas amenable to CO_2 mixed with N_2.

The existing producing areas in the Raniganj South and East blocks are potentially the most attractive, as they have existing CBM infrastructure in place that could be used for ECBM, producers like Great Eastern Energy Corporation Ltd. and Essar Oil with experience, and those are near many potential industrial facilities that would be good sources of CO_2 for developing a CO_2 storage-ECBM project. But, these areas may not be as attractive with regard to the N_2/CO_2 mix in the capture stream, potentially impacting the economics of CO_2 capture.

However, with current CBM activities underway, depending on the geographic location and the local geological characteristics of the target coal seam, these areas could contain good prospects for a commercially viable CO_2 storage-ECBM project. ARI identified a total potential CO_2 storage capacity of 824 million tons in Raniganj (South and East), Sohagpur (East and West), Parbatur Area, and East Bokaro (ARI 2015, exhibit 17).

5 Conclusions

India has the coal resources, energy demand trajectory, and experience to implement a synergistic set of technologies that would allow responsible expansion of fossil fuel use while demonstrating leadership in both CCUS and ECBM. As much as an additional 20% of the coal field methane in place in India is estimated to be recoverable through the application of CO_2-ECBM techniques. Oxy-combustion technology developed by Jupiter Oxygen promises to be a cost-effective partner in such a development. First mover carbon capture projects can be supported through the CCS Trust Fund that is administered by the Asian Development Bank and the World Bank Group. The Green Climate Fund should support accelerated carbon capture project deployment in emerging economies that are heavily dependent on coal consumption for economic growth in the coming decades.

In principle, the synergies between oxy-combustion and ECBM could allow coal-fired power plants to clean up their emissions at reasonable cost. CO_2 revenue will strongly depend on suitability and proximity of the CO_2 utilization site. In the case of ECBM, CO_2/N_2 revenue will be a function of the local geology of the coal seam, as well as the CBM infrastructure in place and CBM/ECBM operator's experience.

Significant CO_2 utilization potential, favorable project locations, as well as selecting cost-effective integrated technology systems are necessary for successful implementation of first-of-its-kind carbon capture demonstration projects in emerging economies. CCUS technology deployment in India will enable low-carbon growth based on a cleaner fossil energy strategy.

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Part IV

Current Research and Green Technology Perspective for Industry

Chapter 15
Carbon Dioxide Management—Aluminium Industry Perspective

Anupam Agnihotri, Suchita Rai and Nitin Warhadpande

Abstract Aluminium plays an important part in the development of a country as it has diverse range of applications and utilities. A global warming and greenhouse gases have become key issues for aluminium industry and the industry has committed itself to reduce emissions of greenhouse effect gases in coming years. The CO_2 equivalent per tonne of aluminium can be reduced by lowering the emission of perfluorocarbon (PFC) arising from anode effects and by reducing the energy consumption. Carbon footprint of aluminium industry has been illustrated and sources of carbon emissions have been explained in the paper. Carbon neutrality can be achieved by implementing several R&D measures and enhanced usage of aluminium in various sectors.

Keywords Aluminium industry · Carbon dioxide emissions and its sources · Carbon footprint · Carbon neutrality · Energy and environmental sustenance

Abbreviations

PFC	Per-fluoro carbon
ACD	Anode-Cathode distance
LEED	Leadership in Energy and Environmental Design
NASA	National Aeronautics and Space Administration
EPA	Environment Protection Act

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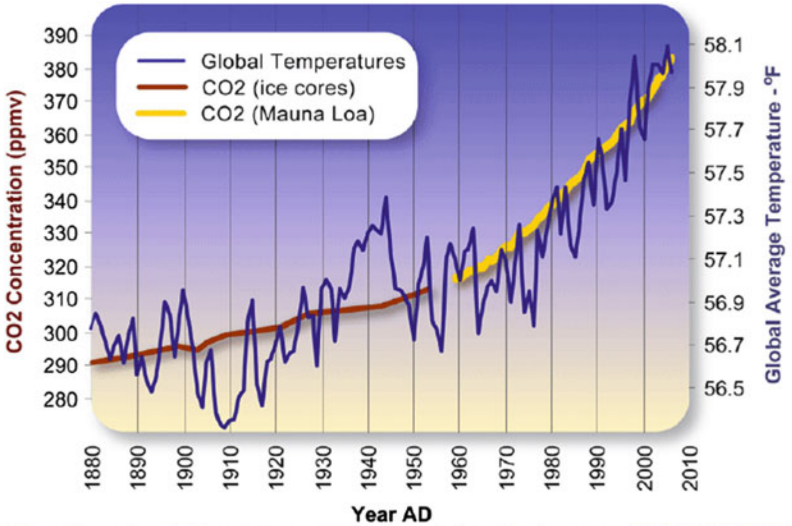

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& http://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_mm_mlo.dat
Graphic Design: Michael Ernst, The Woods Hole Research Center

Fig. 1 Global temperature and CO_2 concentrations

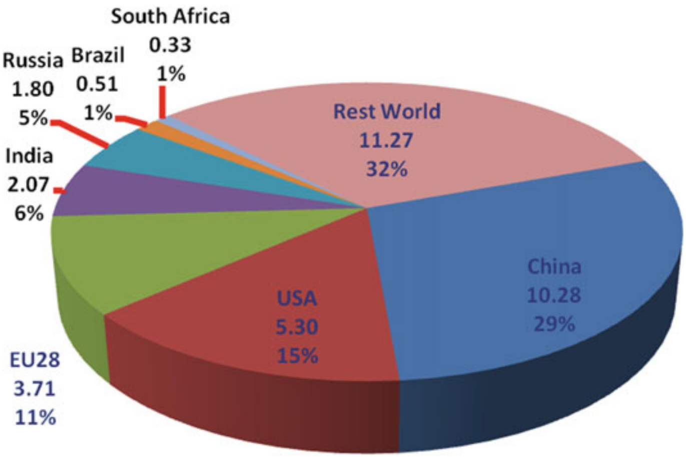
1 Introduction

Aluminium represents the second largest metals in the world and it has played an important role in the development of human society civilization. An estimated 8.3% of the earth crust is composed of aluminium. It is the third most common element after oxygen and silicon. The metal industry contributes about 21% of total global carbon dioxide emissions from all sources, led by iron and steel (4.4%) and aluminium (1.7%) (IPCC 2014). The data from the year 1880 to 2010 show that increased CO_2 concentrations in the atmosphere have lead to the rise in global temperature (Fig. 1).

The world CO_2eq production in the year 2014 was 35.25 Gt and Fig. 2 shows the world contribution towards CO_2 production. Table 1 shows the scenario of direct CO_2 emission from industries in the world across different countries.

2 CO_2 Emission in Aluminium Production

Primary aluminium production is the largest source of emissions of two PFCs, i.e. tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6). Primary aluminium producers are already setting an example for other industries by taking steps to evaluate and reduce emissions of one of the most potent greenhouse gases, i.e. perfluorocarbons



Emission Data Base For Global Atmospheric Research, 2014 Report

Fig. 2 World contribution towards CO_2 production (Emission Data Base for Global Atmospheric Research 2014)

Table 1 Contribution of country wise direct CO_2 emission from industry

Country	% of World 2002	% Change	
		1990–2002	Projected 2002–2020[a]
China	24.7	21	22
EU-25	14.2	−15	4
United States	12.8	−10	12
India	5.5	49	65
Japan	5.5	2	–
Russia	4.4	−19	44
South Korea	2.2	77	–
Brazil	2.2	61	65
Canada	1.8	3	–
Indonesia	1.7	152	54
Mexico	1.2	−26	49
Australia	0.8	−18	21
World	100.0	18	26

Source Compiled by authors from various sources

Note This table combines IPCC source/sink categories 1A2 (manufacturing and construction) and 2 (industrial processes). Growth rates for Russia are from 1992 (not 1990)

[a] Projections are drawn from IEA (2004) and include only CO_2 from fossil fuels. The projected figure for U.S. includes Canada; Australia includes New Zealand

"–" Signifies no data

(PFCs). The perfluorocarbon emissions are related to the “anode effect” and have a high global warming potential (GWP) of 6500 (CF_4) and 9200 (C_2F_6) (EPA 1999).

2.1 *Carbon Footprint of Aluminium Industry*

The aluminium industry worldwide produced 53 million tonnes of material in 2014, a mere about 3% of the total volume produced by the iron and steel industry. Although the carbon footprint of the iron and steel industries is about three times larger than that of the aluminium industry, unit carbon emission for the aluminium industry (12.7 metric tonnes of CO_2eq per tonne) is about 13 times greater than that of iron and steel. Table 2 shows the Global Metal Industry carbon footprint for the year 2008 while Table 3 depicts the carbon footprint for aluminium industry (MBE 2010).

The current carbon footprint of the global aluminium industry is estimated at 500 million metric tonnes carbon dioxide equivalent (CO_2eq), representing about 1.7% of global emissions from all sources. Figure 3 shows the green house gas emissions by different industries and the industrial data for the year 2014 was 12.7Gt (EDBGAR 2014).

Table 2 Global metal industry carbon footprint (year 2008)

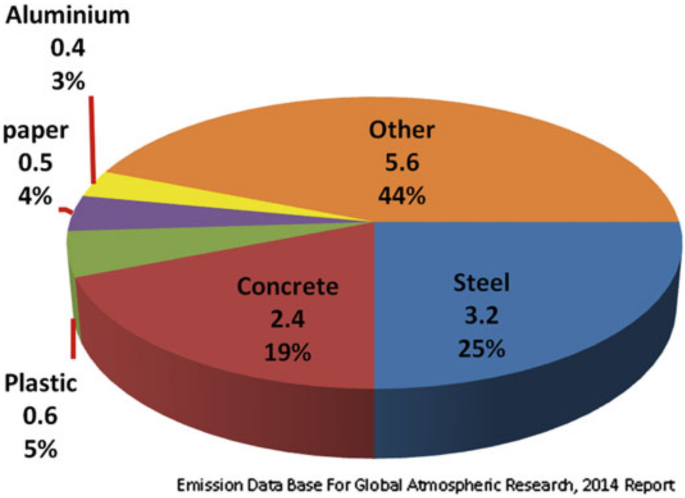
Metal	World Production	CO_2eq (Mt/Mt)	% Global GHG
Iron and Steel	1330	1.0	>4
Aluminium	38	12	>1
Copper	17	5.5	<1
Zinc	10	3	$\ll 1$
Magnesium	1	>18	$\ll 1$
Titanium	0.1	>20	$\ll 1$

Source International aluminium conference

Table 3 Carbon footprint of the global aluminium industry (year 2008)

Items	Production (MMT)	Unit emission CO_2eq (Mt/Mt)	Total emission Mt CO_2eq	Comments
Smelting	38	10	380	World average
Anode effect (PFC)	38	2	75	0.3 kg/Mt GWP = 6500
Recycling	40	0.5	20	5% of Primary
Total emission			475	1% of Global 44.130 Mt CO_2eq

Source International aluminium conference



Emission Data Base For Global Atmospheric Research, 2014 Report

Fig. 3 Green house gas emissions for different industries

2.2 *Sources of Carbon Emissions in Aluminium Industry*

The carbon-based emissions associated with the aluminium production come from the following sources:

(i) Bauxite mining: 2–3 tonnes of bauxite yield one tonne of alumina. More than 250 tonnes of bauxite is mined annually. 150 MJ primary energy consumed per dry tonne of bauxite which produces 20 kg CO_2eq per tonne of aluminium produced.

(ii) Alumina refinery: Fuel combustion for heat and steam represent the bulk of Bayer process emissions, with 10% from indirect sources. In the Bayer process of refining bauxite two tonnes of alumina yield one tonne of aluminium. 15,000 MJ primary energy is consumed per tonne of metallurgical alumina. All this amounts to about 1000 kg CO_2eq per tonne of aluminium produced.

(iii) Anode production: The carbon anodes consumed in the Hall–Heroult Process are often baked before use (Prebake technology) in gas- or oil-fired furnaces. Around 430 kg of anodes are used to produce 1 tonne of molten aluminium. 4000 MJ primary energy consumed per tonne of anodes produced. This produces about 200 kg CO_2eq per tonne of aluminium produced.

(iv) Reaction products: CO_2 from anode consumption now constitutes around two-thirds of the process direct emissions, with PFCs making up the remainder. The reaction produces oxygen that reacts with the carbon anode to produce CO_2 and small quantities of CO; this reaction produces about 1500 kg of carbon dioxide equivalents for each tonne of aluminium produced. Total absolute direct GHG emissions from electrolysis are today 35% below 1990 levels despite a tremendous increase in primary aluminium production capacity over the years. This has been driven by a reduction in the emissions of perfluorocarbon gases (PFCs) by more than 90% per tonne aluminium between 1990 and 2013.

(v) Air burning: The carbon anode loses mass to oxidation with the atmosphere which produces 0.130 kg of CO_2 for each kilogram of aluminium produced.

(vi) Electricity Generation and Transmission: Global average smelter electrical (AC) power consumption is in the range 14–15 MWh per tonne of aluminium. Potlines operating on electricity obtained from coal-fired power plants produce 16.0 kg of CO_2 gas for each kilogram of aluminium produced, while potlines using electricity from hydropower plants produce close to zero CO_2 gas emissions.

(vii) Ingot casting: Molten aluminium, along with process scrap, is cast into primary metal products, for which heat is required. GHG emissions from cast-houses constitute both direct sources of fuel combustion (66%) and indirect sources from electricity consumption. 10,000 MJ of primary energy are consumed per tonne of aluminium ingot. During this process about 90 kg CO_2eq/tonne of aluminium is produced.

(viii) Semi fabrication: Primary and recycled aluminium ingots are reheated and reformed into semi-fabricated products sheet for aircraft, foil for packaging, extrusions for windows, castings for cars and buses. Each process has a different energy and emissions profile, but the average GHG emissions are around 800 kg CO_2eq per tonne of product.

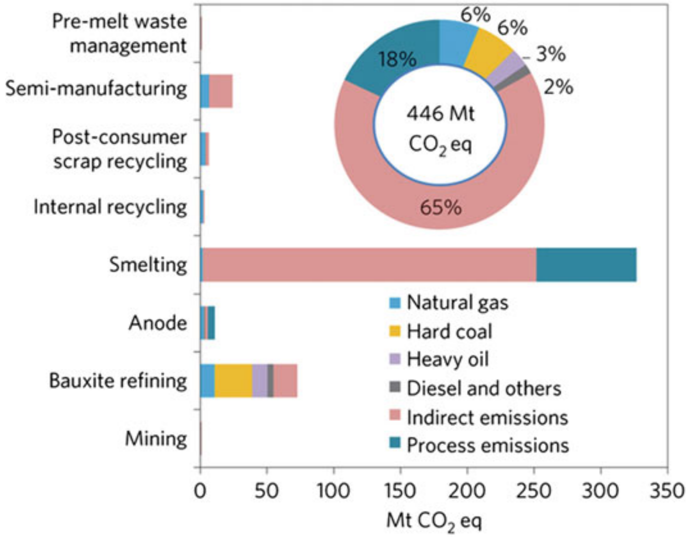


Fig. 4 Contribution of different carbon emitting sources in an aluminium industry (http://www.nature.com/nclimate/journal/v3/n4/abs/nclimate1698.html)

(ix) Recycling: It requires only 5% of the energy required for primary aluminium production. Recycling avoids the process emissions associated with primary production and produces only 125 kg of CO_2eq/tonne of aluminium.

Figure 4 demonstrates the contribution of different carbon emitting sources in an aluminium industry.

3 Steps Towards Carbon Neutrality in Aluminium Industry

In the twenty-first century, sustainability is widely regarded as the new corporate culture, and leading aluminium industries are striving towards carbon neutrality. For the global aluminium industry, carbon neutrality is defined as a state where the total “in-use” CO_2eq saved from all products in current use, including incremental process efficiency improvements, recycling and urban mining activities, equals the CO_2eq expended to produce the global output of aluminium. Around the world, the aluminium industry is working on the following integrated and quantifiable plan for achieving “carbon neutrality”.

(i) Increase use of green electrical energy grid
(ii) Reduce process energy needs
(iii) Deploy products in energy saving applications
(iv) Increase in recycling of aluminium
(v) Use of aluminium-intensive efficient machinery in industry
(vi) Efficient aluminium cabling, turbines, solar panels
(vii) Consumer durables and intelligent control systems in energy supply networks
(viii) Lightweight vehicles
(ix) Green buildings
(x) Protective aluminium packaging.

Since it takes 20 times more energy to make aluminium from bauxite ore than to recycle it from scrap, the global aluminium industry is on the verge of setting up reasonable, self-imposed energy/carbon neutrality goal to incrementally increase the supply of recycled aluminium for every tonne of incremental production via primary aluminium smelter capacity. Furthermore, the aluminium industry is striving to take a global leadership position by actively developing internationally accepted and approved carbon footprint credit protocols.

Table 4 Smelting electricity sources and their CO_2 emissions/kg of aluminium

Smelting electricity source	Total GHG emissions (Kg CO_2eq/kg Al)	Change (%)	Where
Hydro	6	−50	Quebec, Norway
Average grid	12	0	World
Natural gas	13	8	Middle East
Heavy oil or coal	16	33	China

Metals Bulletin Event (2010)
Source Das (2012)

3.1 Increase Use of Green Electrical Energy Grid

The electrical grid in the average aluminium production facility emits 12.7 kg of CO_2 for every kilogram of aluminium produced. Facilities that burn fossil fuels such as coal (as in China) often emit as much as 16 kg of CO_2 for every kilogram of material produced a 26% carbon increase. Natural gas burning facilities, such as those in the Middle East, use only 13 kg of CO_2, an increase of only 2%. Use of clean, efficient power sources, such as nuclear (as in Western Europe) or hydro (as in Iceland, Canada, and Brazil) reduces CO_2 emissions. On average, facilities that use nuclear or hydroelectric power sources only emit about 6.2 kg of CO_2eq per kg of material produced, about half of the amount generated by the common electrical grid-powered facility (Das 2012).

The trend towards use of “greener” electricity sources is fairly negative as most newer smelting plants are being built in China (with coal-fired power plants) and the Middle East (with natural gas-fired power plants). A reasonable goal in the long term should be to increase use of “greener” energy sources (hydro or nuclear from coal) by 15%, eliminating 27 million tonnes of CO_2eq emissions a year. Table 4 shows the electricity source with the total green house gas emissions per kg of Aluminium.

3.2 Reduce Process Energy Needs

The aluminium smelting industry has made a significant reduction in its greenhouse gas (GHG) footprint over the past decade. This has been achieved almost entirely by a reduction in the anode effect contribution via perflourocarbon (PFC) gases, and to a lesser extent by the dilution of older, less efficient smelters, as new smelters are brought on stream. The process improvements in the existing technologies, including the minimization of anode effect, and implementation of new technologies can assist in achieving the goal as follows:

(i) Process improvements for existing technologies

- Replace rotary with fluid bed calciners
- Reduce electricity needed for smelting
- Lower anode effect
- Decrease carbon anode consumption

(ii) Development and adaption of new technologies

- H–H centre break prebake at 4.5 cm anode–cathode distance (ACD)
- Wetted drained cathode at 2 cm ACD
- Wetted cathode and inert anode at 2 cm ACD
- Carbothermic electric furnace
- Clay carbochlorination and chloride electrolysis
- Inert Anode Cells (Oxygen Evolution)
- Drained cell technology.

3.3 Increase in Recycling of Aluminium

Overall, the entire process of transforming raw bauxite into aluminium is incredibly energy intensive, requiring copious amounts of electricity, water and resources to produce (that is the main reason why power plants are built solely to support the aluminium industry).

The Environment Protection Act, USA suggests that the releases of per fluorocarbons during the aluminium smelting process are 9200 times more harmful than carbon dioxide in terms of their affect on global warming. Compared to producing virgin aluminium from raw bauxite, recycling old aluminium consumes just 5% of the energy and releases a mere 5% of the greenhouse gases. Infinitely recyclable, aluminium loses none of its integrity even when it is melted down repeatedly, plus, the whole recycling process can be achieved in less than 60 days flat.

Landfills across the globe continue to be the final resting place for infinite numbers of aluminium beverage cans, which, when incinerated, contaminate air with toxic compounds and take up to 500 years to fully decompose. By recycling already-manufactured aluminium materials, precious space can be conserved in landfills and no new waste materials are produced (http://recyclenation.com/2010/11/aluminium-extraction-recycling-environment#sthash.NKgC5POM.dpuf).

3.4 Use of Aluminium-Intensive Efficient Machinery in Industry

There is the great potential for aluminium products, through their production, use, and value recovery (recycling), to reduce both resource use and environmental impact and to increase human well-being and economic activity, and thus to increase the potential for both resource and impact decoupling. However, reduction of anthropogenic greenhouse gas emissions through the use of aluminium-intensive, efficient machinery in industry applications such as, efficient cabling, turbines, solar panels, consumer durables and intelligent control systems in energy supply networks; lightweight vehicles; green buildings and protective aluminium packaging that preserves agricultural outputs actually has far greater potential for achieving sustainability than improvements in energy efficiency within the aluminium smelting processes.

3.5 Lightweight Vehicles

Independent studies have confirmed that aluminium in automobiles has a 20% smaller life cycle CO_2 footprint than steel. Compared with today's steel cars, a fleet of aluminium vehicles saves the equivalent of 44 million tonnes of CO_2 emissions. Aluminium's use in autos and commercial vehicles is accelerating because it offers the fastest, safest, most environmentally friendly and cost-effective way to increase performance, boost fuel economy and reduce emissions while maintaining or improving safety and durability. Nearly 90% of automotive aluminium scrap can be recovered and recycled. Also an aluminium-intensive vehicle can achieve up to a 20% reduction in total life cycle energy consumption and up to a 17% reduction in CO_2 emissions. The advancement of aircraft and rocket technology is directly tied to the advancement and production of aluminium alloys. From the Wright brothers' use of aluminium in the engine of their first biplane to NASA's use of an aluminium–lithium alloy in the new Orion spacecraft, aluminium has created the potential for mankind to fly both around the Earth and into space (www.aluminium.org/products-markets) (www.actonsolar.com/index_files/page5234.htm).

3.6 Green Buildings

Aluminium is superior to steel and iron in its ability to reflect the infrared (heat) rays of the sun. Properly coated aluminium roofs can reflect up to 95% of the solar energy that strikes them, dramatically improving energy efficiency. Aluminium is a key component in LEED-certified green buildings. Use of aluminium helps building projects qualify for green building status under the Leadership in Energy and Environmental Design (LEED) standards which helps in providing insulation and allows daylight and fresh air into buildings. Strengthened alloys can support large glass structures and solar panels (www.aluminium.org/sustainability/aluminium-green-buildings). Figure 5 illustrates the energy savings in reused and reprocessed aluminium as compared to the steel reinforcement and glass products (www.actonsolar.com/index_files/page5234.htm).

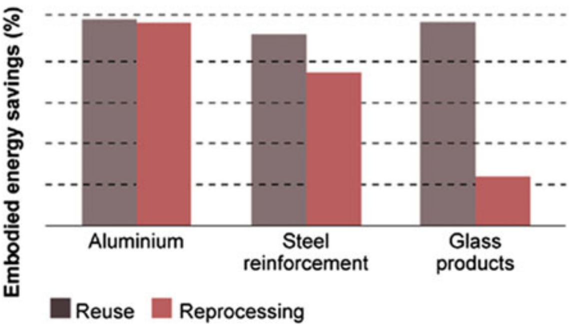


Fig. 5 Energy saving in aluminium as compared to steel and glass products

3.7 *Protective Aluminium Packaging*

Aluminium foil provides a complete barrier to light, oxygen, moisture and bacteria. For this reason, foil is used extensively in food and pharmaceutical packaging. Aluminium foil is also used to make aseptic packaging. This type of packaging enables storage of perishable goods without refrigeration.

4 Sustained R&D Need of the Hour

The environmental driver is linked to the carbon oxide and other greenhouse emissions. On a tonnage basis, the amount of carbon oxide produced is greater than a tonnage of aluminium metal produced. However, the only alternative to carbon oxide is electricity, since a form of energy is always required for metal production. With incremental electrical energy usually being generated by inefficient combustion processes, the potential for reducing the greenhouse impact depends on how electricity generation is accounted.

In the last 25 years, there has been sustained R&D on alternative processes for reduction in process energy needs, which are as follows:

- *Drained cell technology*: Cathode sloping and coated with aluminium-wettable TiB_2. By eliminating metal pad, anode–cathode gap could be halved to ~25 mm, enabling substantial voltage lowering. Other basics would remain the same as present technology
- *Inert Anode Cells (Oxygen Evolution)*: Eliminate consumable carbon anode by having an electrode material that evolves oxygen. Although the electrochemical potential would increase by 1 V ($E^\circ \sim 2.2$ V), the voltage increase would be (hopefully) less because of lower Anode polarization ($\Delta_{\mathrm{min,electrolysis}} = 9.26$ kWh/kg). The superstructure of the existing cell could be refined, reducing capital costs. If drained-cell materials development were successful, further design options are possible.

- *Chloride Process*: Aluminous material converted to (anhydrous) $AlCl_3$ of adequate purity. $AlCl_3$ electrochemically decomposed in a multielectrode cell at ~700 °C ($E^\circ \sim 1.8$ V, $\Delta_{\text{min,electrolysis}} = 6.34$ kWh/kg). Electrochemically generated chlorine is recycled.
- *Sulphide Process*: Aluminous material converted to (anhydrous) Al_2S_3 of adequate purity. Aluminium sulphide electrochemically decomposed to recyclable S2 and aluminium ($E^\circ \sim 1.0$ V) in a multipolar ($\Delta_{\text{min,electrolysis}} = 5.24$ kWh/kg) cell.
- *Carbothermal Reduction*: Convert aluminous material to an intermediate Al_4C_3 (or oxycarbide) chemically at $T > 1700$ °C. React carbide with further oxide to evolve CO and produce aluminium (or alloy) at $T > 2000$ °C. Refine the metal quality to a usable grade ($\Delta_{\text{minimum}} = 9.0$ kWh/kg).

5 CO_2 Utilization for Neutralization of Red Mud

The large amount of energy needed in the aluminium production is met through the captive coal-fired power plant in India, which results in associated high levels of CO_2 greenhouse emissions. There is high potential for capturing carbon dioxide and mixing it with bauxite residue (red mud), a waste from Bayer process would lock up large amounts of the greenhouse gas that otherwise would be released into the atmosphere. The process of carbon capture and storage, where carbon dioxide is removed from flue gases before being stored in underground reservoirs is called as carbon sequestration. Red mud contains high level of alkalinity with a pH value of about 13. The present worldwide generation of red mud is ~75 million tonne of which ~4 million tonne of red mud is generated annually in India. The use of carbon dioxide from the atmosphere or from industrial emissions is potentially significant source of acid for neutralizing red mud. In India, using CO_2 in sequestration of red mud has been investigated by some researchers (Sahu et al. 2010; Rai et al. 2013). As such no industrial application of utilization CO_2 from aluminium industry is in existence.

6 Conclusion

In the recent years, the aluminium industry sector is committed to reduce emissions of greenhouse effect gases. For this to actually be implemented, a plethora of measures as comprehensively explained in the paper have to be taken up and carbon footprint has to be reduced. New technologies and alternative processes have to be developed for proper management of carbon dioxide in aluminium industry. R&D in the production methods and more use of aluminium in various sectors has to be worked upon and explored.

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Chapter 16
Bioenergy Combined with Carbon Capture Potential by Microalgae at Flue Gas-Based Carbon Sequestration Plant of NALCO as Accelerated Carbon Sink

Ranjan R. Pradhan, Rati R. Pradhan, Siddhanta Das, Brajesh Dubey and Animesh Dutta

Abstract Microalgae with its numerous applications such as food, dietary supplement, fuels, and materials in environmental biotechnology are being regarded as a priority area for further investigations. National Aluminum Company (NALCO) in India uses coal as source of energy in aluminum production. A pilot project was undertaken by NALCO for carbon capture and storage by using microalgae in their captive power plant at Angul in Orissa. The production of microalgae using industrial emissions enhances the carbon sequestration in addition to the economic benefits of algal cultivation. The algal biomass while being processed for high-value extractives generates the residual biomass as the process waste and needs to be utilized effectively; preferably for renewable fuel or material applications. This paper provides an exclusive comparative evaluation of biomass generation of about 2 tons/year and application for possible types of bioenergy potentials with the carbon sequestered as carbon sink. The important criteria and factors reported are useful for further study on comparative lifecycle analysis.

Keywords Microalgae · Biomass · Carbon sequestration · Biofuels · Hydro thermal liquefaction · Open pond cultivation

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Abbreviation

PAR	Photo-synthetically active radiation
HTL	Hydrothermal liquification
PBR	Photo-bioreactor
TGA	Thermo gravimetric analysis
DTA	Differential thermo gravimetric analyser
FTIR	Fourier transform infrared spectroscopy
HTC	Hydrothermal carbonization

1 Introduction

Today biomass energy (or “bioenergy”) is of increasing interest as a renewable, environmentally friendly alternative to energy derived from fossil fuels (Kadam 2001). Through a variety of processes, biomass can be converted to solid, liquid, or gaseous biofuels. Greater use of these biomass-based biofuels could help to ease society’s dependence on fossil fuels and, in the process, reduce net greenhouse gas (GHG) emissions (Pradhan 2009). In addition to use in creating energy, however, biomass is being increasingly used to make a wide range of renewable byproducts, industrial chemicals, pharmaceuticals, textiles, renewable materials, personal care products, and other manufactured.

Natural carbon sequestration process of photosynthesis has long been recognized as a means, at least in theory, to capture anthropogenic carbon dioxide. Photosynthesis is the original process that created the fixed carbon present in today’s fossil fuels. Aquatic microalgae are among the fastest growing photosynthetic organisms, having carbon fixation rates an order of magnitude higher than those of land plants. Microalgae utilize CO_2 as one of their main building blocks and algal photosynthesis may be a viable option for anthropogenic CO_2 capture and sequestration (Cuellar 2015). Effectiveness of the microalgae in producing bio-oil was so promising that it soon found a discrete new category, named as “Third Generation” bio fuel (Dragone 2010).

Adoption of direct feeding of most biomass feedstock in a coal fired boiler to produce heat and electricity has a number of limitations such as high moisture contents, huge investment on the transportation, storage problem due to biological degradation, poor grindability, low energy/bulk density, and lower heating value (Acharya 2015). Despite of being low carbon alternative, bio fuel still is not carbon neutral. Also the effect of using land on environment, high thermal variation and leakage throughout the process, termed as carbon sink have to be taken care of (Grierson 2013). The most noticeable disadvantage of microalgae is the biofuel we get from it is slightly unstable than the rest of the feedstock. For that we have to use certain chemicals to stabilize the bio-oil. Hence it is necessary to calculate all the potential impact of the whole process of producing bio-oil from microalgae using power plant flue gas to check its sustainability (Liu 2013).

The project undertaken by National Aluminum Company (NALCO) for the first time in India at a commercial establishment having a goal: to initiate aggressive carbon capture and sequestration for coal-generated electricity in Orissa. The concept of using microalgae to mitigate CO_2 emissions from stationary combustion sources is not new. The use of algae to capture carbon dioxide from power plant emissions deserved further research because of the co-benefit that results from the production of biofuel and bio products (Choudhary 2015). While microalgae culturing is expensive, microalgae can also produce a variety of high value compounds that can be used to generate revenues. The microalgae cultivation subsequently results in generating biomass and therefore a high carbon containing material for further renewable applications (Pradhan 2013; Zhang 2015). Those revenues could pay for the cost of carbon capture and sequestration (Guo 2015).

The Pilot-cum-demonstration project was undertaken by NALCO for carbon capture and storage by using microalgae in their Captive Thermal Power Plant (CTPP) at Angul. The CO_2 emitted from the stacks was adopted in the system and injected into shallow water ponds to expedite growth of cultured microalgae. The objective of the pilot project is to; (a) erect a mass cultivation system for

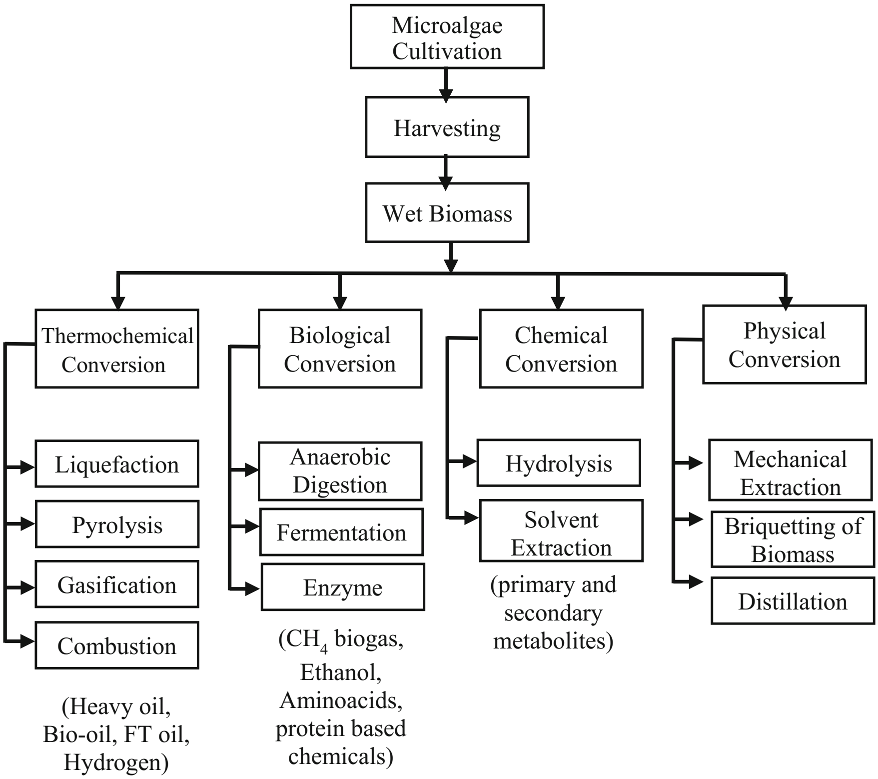


Fig. 1 Flow chart for possible bioenergy production from algal biomass

microalgae, feeding on CO_2 from flue gas of thermal power plants, (b) demonstrate carbon capture from the flue gas emitted from thermal power plants to generate micro-algal biomass, (c) harvest biomass generated in the process, (d) evaluate the potential of value addition to the biomass generated for different applications, and (e) quantitatively tons sequester CO_2/acre/year.

Microalgae biomass generally consists of protein, carbohydrate, and lipid. Many thermochemical and biochemical conversion of microalgae biomass generates range of bioenergy products as shown in the Fig. 1. Total process can be classified into three major operating parts. First flue gas, generated from power plant is brought to open culture pond after heat exchange, then the microalgae biomass is cultivated using CO_2 from flue gas, then the cultivated biomass is harvested to recover biomass as a intermediate product and finally that cultivated microalgae is used to produce bioenergy products using various processes.

With this report we evaluate the potential bioenergy value chain, environmental impact and the sustainability of biofuels obtained from microalgae generated at this pilot plant. The reported outcomes contribute to the methods to verify potential impacts and evaluate carbon footprint of the process and provides information to producer, supplier, and user, where it requires changing in the process in terms of GHG emission reduction.

2 Materials and Methods

2.1 Cultivation of Algal Biomass

Microalgae cultivation has to meet the criteria such as, availability of sunlight throughout the year, favorable climatic conditions, temperature, relative humidity, precipitation and evaporation, land topography and access to nutrients, carbon sources and water. Algae convert solar energy into biomass by oxygenic photosynthesis in a natural condition at a photosynthetic efficiency of 4–6% Algae absorb sunlight in the wavelength ranging from 400 to 700 nm for photosynthesis which is only 47% of total energy from the sun (Sudhakar 2012). Photo synthetically Active Radiation (PAR) varies with latitude, seasonality and geographical factors. Photosynthetic organisms use eight photons to capture or fix one molecule of CO into carbohydrate (CHO) n (Raven 2013). Odisha receives an average solar radiation of 5.5 kWh m^{-2} and around 300 clear sunny days every year (Tarai 2016). Therefore, Odisha with its existing solar radiation conditions offers rich potential for microalgae production (Lakshmi 2015).

Open culture pond system is relatively economical than other Photo Bioreactor (PBR) systems because of easy maintenance and low energy demand. It can be set up in nonagriculture lands but productivity efficiency, gas mixing conditions are lower along with limited illumination sourced from solar irradiation. However, modified pond cultivation is a better option for economical and operational issues as demonstrated with the establishment of pilot plant for evaluation. Microalgae strains are collected and selectively enriched. These blue—green algae were adopted at the flue gas fed carbon sequestration plant of NALCO, Angul, India, in a modified open raceway pond system. The isolated stabilized cultures were identified to be of *Leptolyngbya/Pseudophormidium* sp. with 16S/18S rRNA analysis and were further monitored routinely by optical and biomass characterization. The biomass recovery rate of 23 ton/acre/year achieved initially by the pilot plant and was accepted as the yield of the system for further calculation purpose. All the input inventory data on the cultivation components and HTL process are assessed, calculated or adopted as per scientific literature and recorded.

Flue gas inherently has higher temperature. For cultivation purpose it is processed through heat exchanger and the recovered heat from this process is used further to dry the algal biomass slurry collected from pond. The CO_2 and other components are then transferred to cultivation pond to use as feed for algal growth. The mass transfer of CO_2 is depending upon solubility of gas and/or the solubility of other gases mixed in the flue gas and water chemistry. Mass transfer can be achieved via carbonation sump or gas injection process, etc. In phototrophic growth condition, algal biomass absorbs sunlight as an energy source, assimilate CO_2, N, P, and other nutrients to replicate and grow faster. The production rate can be enhanced by changing the culture environmental conditions. Microalgae can be harvested by centrifugation, filtration, gravity sedimentation, or flocculation (Grima 2003). The step of this process begins with cultivation of microalgae using appropriate microalgae strain to culture, which depends on a number of factors like growth rate, composition profiles, temperature, water chemistry, flue gas composition, and so on.

The cultivation system was organized to introduce the necessary nutrients with the attached carbonation stage. Cultivation was done in Photobioreactor (PBR) using a modified open culture pond with supply of CO_2 and other flue gas components. The shortfall in nutrients was provided using commercial nutrient media of Indocan Technology Solutions, Cuttack, India. After harvesting wet biomass with 70% water content as slurry, the biomass was dried using the recovered heat from the heat exchanger and the condensate was recycled to the pond with a 5% operative loss in addition to evaporation loss from the pond. Hydrothermal Liquification (HTL) process does not really require dry biomass as algal biomass slurry can directly be used in this process. But pyrolysis process strictly needs dried biomass. Further drying is therefore done in trays at the heat exchanger cum dryer, however, industrially in larger scale may be done by rotary drum method, which requires an energy intake as much as 7.76 MJ per kg of microalgae (Bennion 2014). The hydrothermal carbonization (HTC) was carried out under moderate temperature as an indicator for potential biochar production and the products were accessed.

2.2 Process Input Inventory

The goal adopted to assess the potential environmental burden and impact of targeted bioenergy for bio-oil production using power plant flue gas through hydro thermal conversion process at the NALCO's algal biomass plant. The scope of this study was a gate-to-gate system boundary, mainly the manufacturing process and coproducts were subjected to this study for potential impact of the input and output materials from the flow. The raw material procurement and end of life treatments of the resources are not subjected to this study. Case study scenario was based on an algal biomass plant, where $\sim 15\%$ carbon dioxide (CO_2) present in the flue gas of coal power plant used for cultivate microalgae in an open culture pond with a heat recovery system and using that recovered heat to dry microalgae slurry with 70% water content. After collecting and drying the algal biomass, this biomass is used to generate bio-oil through HTL process. Electric load used for microalgae cultivation with 3 HP electric power load.

Theoretical calculation was based on local scenario assuming growth of microalgae follows phototrophic pathway, using sunlight as the sole energy source, absorbance of sun light uniformly and stable climatic conditions. The solar energy potential was estimated with the recorded historical climatic conditions of the region. For the process of input data collection was accommodated in three stages: Flue gas to culture pond, cultivation of algal biomass and microalgae to bio-oil. Flue gas generated from this power plant cannot be used directly to the culture pond due to its high temperature. After collecting this flue gas through pipelines, it is directed to a scrubber heat exchanger. Hot flue gas of 140 °C is directed to Scrubber heat exchanger, where it is mixed with cold water of 25 °C and generates a flow of 40 °C containing flue gas composition. The heat recovered by this process is further used in drying the biomass. The electrical load of the heat exchanger is equivalent to a 1 hp fan and 0.5 hp pumps. This process is further used as two different processes using cold air and using cold water. For air system, input flow rate of cold air is 2170 kg/h with 100 kg/h flue gas. For water system, input rate is 520 kg/h of cold water with 100 kg/h flue gas. After recovering the heat, this water/air with 13% CO_2 is injected in to the open culture pond. The heating (calorific) value of the sample is of great importance for its application as fuel. Heating values was experimentally determined using IKA C200 bomb calorimeter (Wilmington, NC, USA).

2.3 Thermo Gravimetric Analysis (TGA)

TGA study of the biomass was carried out to evaluate the thermal decomposition and fuel fees stock potential. A model Q50 TGA (TA Instruments, New Castle, Del.) was used for the TGA tests. Thermo gravimetric analysis (TGA) was carried out using simultaneous Differential Thermo gravimetric Analyser (DTA) equipped with precision temperature measurement a microbalance at heating rate of 10 °C min^{-1} with a sample of approximately 10 mg. A pair of platinum weight pans (100 μg) was used for containing the samples. Microalgae samples were heated to 900 °C at a rate of 5 °C min^{-1}, and resulting volatile products were analyzed with Thermal Analysis Universal software (TA Instruments, New Castle, Del.).

2.4 Thermogravimetric Analysis Coupled to Fourier Transform Infrared Spectroscopy (TGA-FTIR)

The TGA-FTIR experiments were carried out to obtain three-dimensional plot of the spectra from the gas volatized during the thermal degradation of algal biomass in oxidative atmosphere during a heating rate of 10 °C min^{-1} (TGA/FTIR, Thermo Scientific). The spectral region of the FTIR was 400–4000 cm^{-1} and spectrum scan was conducted with 0.2 s intervals.

3 Results and Discussion

Microalgae Biomass Productivity Potential

Microalgae Production (g/m^2/day) is given by following Eqs. 1–4

$$\text{MB}_{\text{production(daily)}} = \frac{\eta_{\text{transmission}} * \eta_{\text{capture}} * s_I}{E_{\text{microalgae}}} \tag{1}$$

where: $\text{MB}_{\text{production(daily)}}$ is microalgae productivity in g/m^2/day, $\eta_{\text{transmission}}$ is the efficiency of light transmission to microalgae, η_{capture} is the efficiency of conversion of incident sunlight to biomass in microalgae, S_I is the solar Irradiance falling on a horizontal surface (kWh/m^2/day), and $E_{\text{microalgae}}$ is Energy stored in the biomass (MJ/kg).

$$E_{\text{microalgae}} = f_L * E_L + f_p * E_p + f_c * E_c \tag{2}$$

where f_{L} is a microalgae lipid fraction usable for biodiesel, f_{P} is microalgae protein content fraction, and f_{C} is the microalgae carbohydrate content fraction

$$\eta_{\text{transmission}} = \eta_{\text{lightdistribution}} * \eta_{\text{land}} * \alpha * PAR \tag{3}$$

and

$$\eta_{\text{capture}} = \eta_{\text{photosynthesis}} * \eta_{\text{photoutilization}} * (1 - r) \tag{4}$$

where: η_{capture} is the efficiency of conversion of incident sunlight to biomass in microalgae, $\eta_{\text{photosynthesis}}$ is photosynthetic efficiency, $\eta_{\text{photoutilization}}$ is the fraction of captured photons utilized by microalgae and r is the fraction of energy consumed by respiration in microalgae.

Based on the above mathematical equations:

Theoretically maximum annual biomass productivity is calculated to be of 291.5 ton/ha/year based on the historical radiation availability under the meteorological conditions of Bhubaneswar. With this potential output, a productivity may be easily targeted at a sustainable yield of 20% of the theoretical.

The inventory of all the processes in the open pond system for cultivation is as listed in Table 1.

Considering the flue gas outflow from stack, using it as a raw material for growth of microalgae, open culture pond uses a heat exchanger to recover excess heat and finally using it to dry algal biomass, the input inventory was established and is as listed in Table 2. The comparative fuel characteristics of the algal biomass are presented in Table 3.

The various products generated at the algal biomass generation facility at NALCO are as shown in the Fig. 2. The major commercial grade products were fertilizer, adsorbent, bio-based and biodegradable composites, and bioenergy feed stock.

The FTIR spectroscopy of the processed product after HTC of the biomass was compared with the raw biomass to demonstrate the extent of thermal conversion. As shown in the Fig. 3, the HTC process residue is devoid of most functional groups in the FTIR spectra.

Figure 4 represents the thermal decomposition of the components of the biomass at a constant heating rate under combustion. The weight loss curve and the heat flow trend clearly demonstrate two stages having distinct peak temperature of 337.5 and 442.6 °C during thermal valorization.

Detailed investigation of the kinetics and the ash profile can very useful for designing gasifiers and potential co-firing with coal. The volatile compounds evolved during combustion of biomass were analyzed in real time by FTIR. The

Table 1 Inventory data sheet for pond cultivation operation

Open pond cultivation		
Pond energy intake	3(2 hp fan + 1 hp motor/pump)	Hp
	2.24	kW
CO_2 uptake efficiency	70–90	%
Evaporative water loss	150	cm $year^{-1}$
Operative water loss	0.05	%
Biomass productivity	22	Tons $acre^{-1}$ $year^{-1}$
	18.89	gm m^{-2} day^{-1}
Biomass lipid content	0.1–0.15	%
Cycle period	20	Days

Table 2 Inventory data sheet for flue gas handling to the cultivation system

Step	Value	Unit
CO_2 from flue gas (water)	1.5	hp
Energy intake	1.12	kW
Water	520	kg h^{-1}
Flow in	25	°C
Temperature	298	K
Enthalpy	−7.82	MMBtu h^{-1}
Flue gas	100	kg/h
Flow in	140	°C
Temperature	413	K
Enthalpy	−0.26	MMBtu h^{-1}
CO_2	13	kg/h
N	68.99	kg/h
O_2	4.99	kg/h
CO	0.0004	kg/h
NO_2	0.0045	kg/h
SO_2	0.0012	kg/h
Water	12.99	kg/h
CO_2 from flue gas (AIR)	1.5	hp
Energy intake	1.12	kW
Air	2170	kg/h
Flow in	25	°C
Temperature	298	K
Moisture content	0.13	%

primary valorization of algal biomass in terms of overall mass conversion occurred between 215 and 525 °C. The two stages identified earlier for decomposition also can be noticed as two districts peaks of gas evolution in the similar range in three-dimensional IR spectra. A typical three-dimensional plot of the spectra presents as Fig. 5 obtained from the gas volatized during the thermal degradation of algal biomass in oxidative atmosphere between the wave numbers 400–4000 cm^{-1} at heating rate of 10 °C min^{-1}. The OH peak 3400 and 3500 cm^{-1} is characteristic of water and the source could possibly be moisture with biomass. CO_2 represented by the functional group C=O at the absorption band between 2268 and 2395 cm^{-1} is the highest peak observed in FTIR. The biomass shows an minor absorbance peak in the region of 1600–1800 cm^{-1}, and this could demonstrate the presence of C–O(H) functional group and due to CH_3COOH. Minor absorbance band between 1750 and 1650 with peaks at 1710 and 1740 correspond to C=O carbonyl stretching of carboxylic acid, ketones, ester, or aldehyde groups are also observed but are not significant. Relatively larger peak at 1250 cm^{-1}, the fingerprint region C–O stretching indicate presence of either phenols or lipids (Bassilakis 2002).

Energy sourced from biomass conversion systems can play a role in carbon neutral energy as the emission from biomass energy system results in sequestered

Table 3 Density of algal biomass generated in comparison to other energy materials

Comparison	Algal biomass (NALCO)	Hammer milled woody biomass[a]	Briquettes[a]	Baled corn stover[a]
Bulk density (kg/m^3)	553.05	160	225	200
Energy density (GJ/m^3)	>7.7	3.6	6.4	4.3

[a] Clarke S; fact sheet, biomass densification for energy production, OMAFRA (2015), http://www.biomassinnovation.ca/pdf/Factsheet_OMAFRA_BiomassDensification.pdf

Fig. 2 Products from carbon sequestration plant

CO_2. Algae cultivation from such carbon neutral emission will further sequester carbon from such system and drive towards a carbon negative scenario while generating energy. Therefore, as represented in Fig. 6, such a system will drive a bioenergy system emitting neutral CO_2 wastes streams, to it be treated as a “free” input to a bioenergy and bio refinery process while earning further carbon negative

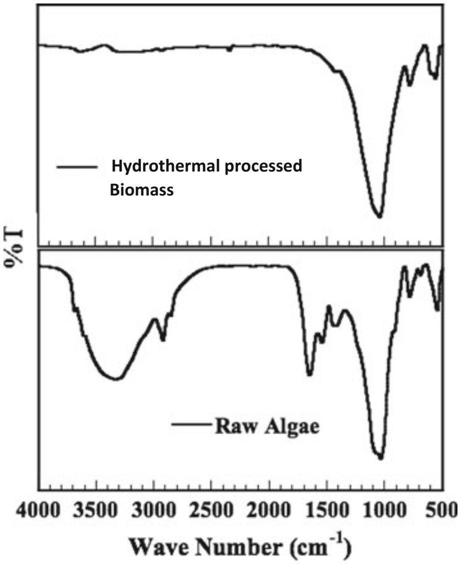


Fig. 3 FTIR of algal biomass and HTC processed biomass

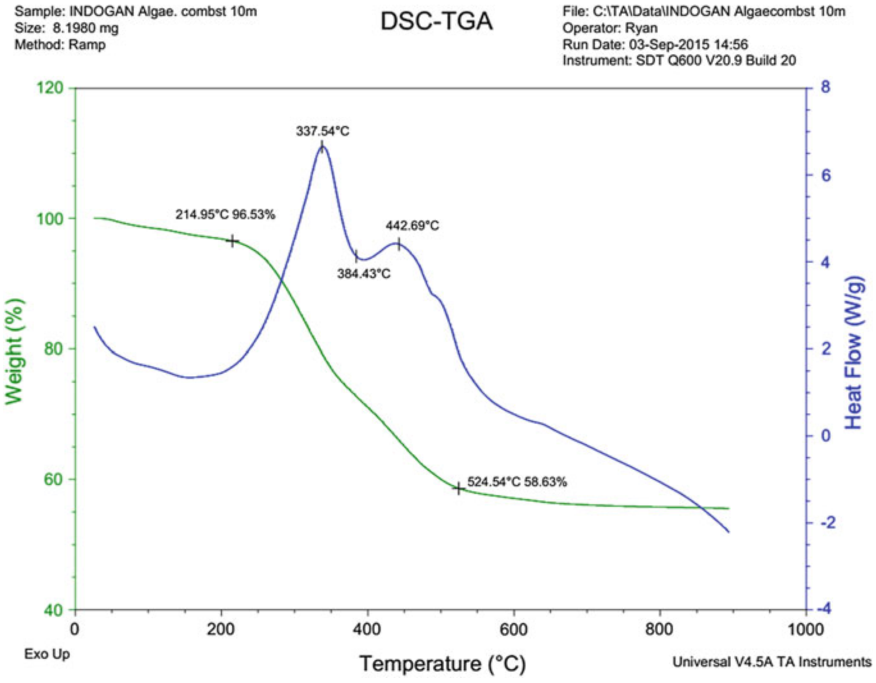
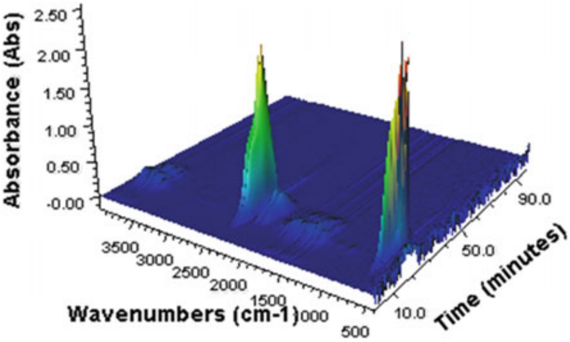


Fig. 4 TGA of algal biomass under oxidative heating rate of 10 °C/min

Fig. 5 Three dimensional FTIR spectra of the gases produced during thermal decomposition of algal biomass in oxidative atmosphere



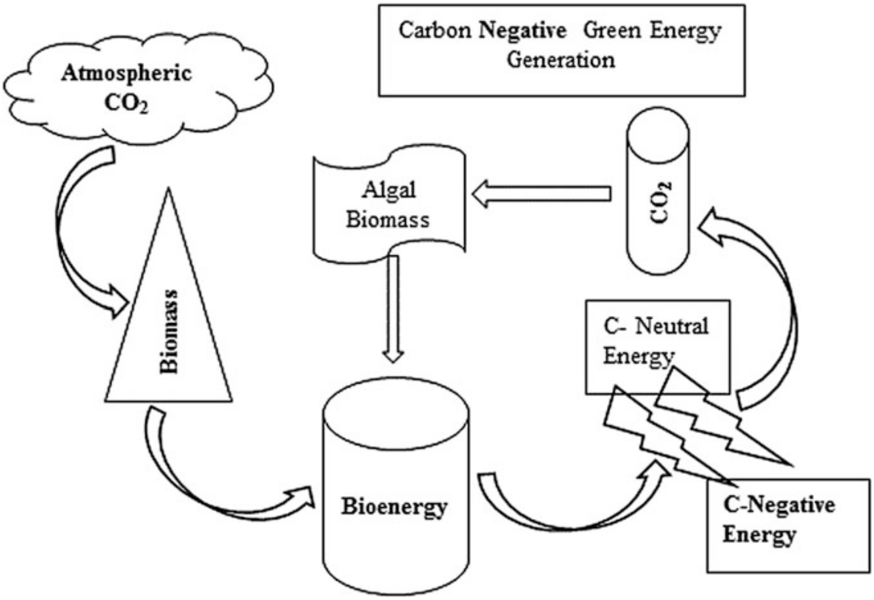


Fig. 6 Carbon negative bioenergy with microalgae cultivation

credits with reduced environmental load. Potential generation of a significant amount of short term carbon negative energy exists till the operation life of a biofuel plant. Further promising application of algal biomass may be exploited for value addition biomaterial application to promote this further. Assessments of the components and energy content of the biomass clearly suggest potential for carbon negative energy generation from about 15% equivalent the sequestered biomass yield with biogas with thermophilic biogas digester system (Pradhan 2009, 2013). Likewise, bio-oil production from the algal biomass results in production of 58% biochar consisting of 30–40% ash and can drive to carbon negative storage by mixing them in soil. United Nations Framework Convention of Climate Change (UNFCCC) included “Biochar” as a potential sequestration tool. If adopted on a large scale, producing biogas and biochar eventually would be a significant carbon sequestration measure (Acharya et. al. 2015).

4 Conclusion

Microalgae are also the most formidable source of bio fuel in terms of sustainability, ability to grow on nonarable land and low emission potential. This study of industrial emissions from an aluminum plant incorporated the experimental and literature data to produce the environmental assessment result and compared it with other more available fuel options, e.g., biodiesel, fossil fuel, etc., and also compared the result with a second conversion pathway and pyrolysis to choose the better one. The harvesting process does not require much energy or chemicals, so impact is much lesser in this part. Also this process incorporated CO_2, which is emitted to the environment from the nearby thermal power plant and used as a food for microalgae. This carbon sequestration process provides a positive impact to environment.

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Chapter 17
Current and Future Trends Toward Reduction of CO_2 Emission from Steel Industries

Santanu Sarkar and Supriya Sarkar

Abstract Carbon dioxide is the major greenhouse gas in the environment. Its largest contributor is fossil fuel based industries and among them steel industry holds one of the vital positions. In view of global climate change agreements, there are efforts to reduce CO_2 emission by development of suitable technologies. In last decades, various technologies have been developed to separate CO_2 from the flue gas of power and industrial plants by using chemical or physical absorption, adsorption, cryogenic methods, membrane systems and biological fixation, etc. This paper elaborates on the aspects of different carbon capture processes and sequestration technologies developed and adopted by steel industries. In many cases, pilot scale studies have been completed successfully and are ready for implementation. Though, further development and fine tuning is required for commercialization of such processes.

Keywords Steel industry · CO_2 emission · CO_2 capture technologies · Commercialization

Abbreviations

WSA	World Steel Association
BF	Blast furnace
EAF	Electric arc furnace
BOF	Basic oxygen furnace
DRI	Directly reduced iron
ULCOS	Ultra-low carbon dioxide steelmaking
PSA	Pressure swing adsorption
ULCOWIN	Ultra-low carbon dioxide electrowinning
COG	Coke oven gas
ESI	Emirates steel industries
ADNOC	Abu Dhabi National Oil Company

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NEDO	New Energy and Industrial Technology Development
ULCOLYSIS	Ultra-low carbon dioxide electrolysis

1 Introduction

The combustion of fossils fuels is the major contributors of greenhouse gases (GHGs) and among all gases, carbon dioxide plays vital role as a GHG. CO_2 emission is mainly caused by three major sectors, i.e. energy, transportation and industries (Fig. 1). Among the industries, the iron and steelmaking industry is the largest industrial sources of CO_2. Approximately, the rate of emission is 1.2 Gt CO_2/year, which is more than 2% of anthropogenic CO_2 emissions around the globe. According to the estimation of World Steel Association (WSA), total 1665 million tones steel has been produced in the year of 2014 whereas production was 1433 million tones in 2010 and thus growing demand of steel production is actually contributing enhancement in CO_2 emission (World Steel in Figures 2015).

Steel production is categorized in two different ways. First, the integrated steel mill in which steel is made by reducing iron ore in a blast furnace (BF) and subsequent processing in a primary steelmaking plant via blast furnace-basic oxygen furnace (BF-BOF) route and second, the mini-mill in which steel is made by melting scrap steel or scraps substitutes in an electric arc furnace (EAF). The integrated steel mills contribute 60% of the global production of iron making process. Besides the above two categories, there are alternative iron and steelmaking processes based on direct or smelting reduction technologies, e.g. COREX,

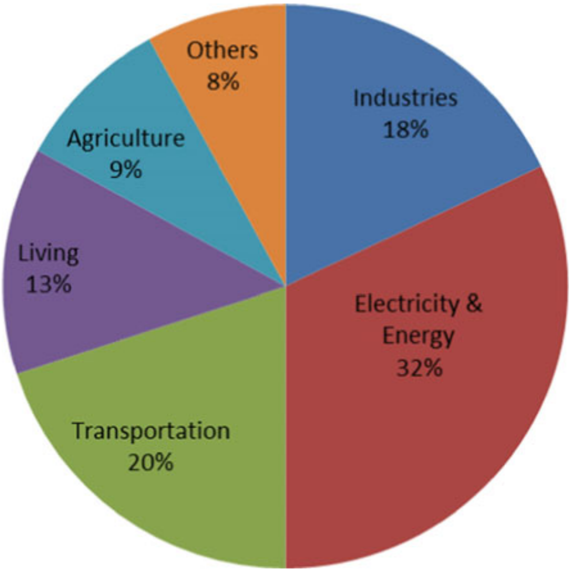


Fig. 1 Global CO_2 emission contribution by different sectors

FINEX, DRI, Midrex, etc., which are also used worldwide for steel production. These technologies have been commercially proven, nonetheless BF-BOF and EAF routes are dominating in steel production since several decades and may be so in next fifty years. The major threat due to emission of CO_2 is very much well known. Therefore, it is the high time to take necessary action against this alarming global warming threat.

In last decades, different CO_2 capture technologies have been developed by researchers and many of them have been tried to commercialize their developments. The common practices to capture CO_2 emitted from different source points are chemical absorption, adsorption, cryogenic separation and membrane based separation (Gabelman and Hwang 1999; Olajire 2010). However, according to Prusty (2008) CO_2 capture and its sequestration or storage will be capable of maintaining long-term isolation of CO_2 from the environment (Wang et al. 2010) called carbon capture and sequestration (CCS). Therefore, to reduce CO_2 emissions from steelmaking industries, one of the leading options has been considered by iron and steel stakeholders is CO_2 capture and storage (CCS). A huge development of this technology is required for adaptation in real scenario inside the steel mills.

The current study aims to highlight the sources of CO_2 in steelmaking process as well as the several aspects of current and future practices in CCS technology.

2 Generation of CO_2 in Steelmaking Process

The iron making process is basically the reduction of iron oxide with help of carbon, thus carbon is the reducing agent which is oxidized to CO_2. Not only iron making process but there are also other processes involved in steelmaking which are responsible for CO_2 emission. Depending on the contribution, the sources of CO_2 can be broadly classified as direct source or major sources and indirect or minor sources (Fig. 2). The detail aspects of CO_2 generation have been elaborated below.

2.1 Major Sources

In a steel mill, some processes contribute maximum CO_2 emission such as iron extraction and steelmaking process. The rate of emission of greenhouse gas is inevitably dependent on the route of steelmaking process. Accordingly 0.4 t CO_2/t crude steel produced from an EAF, 1.7–1.8 t CO_2/t crude steel for the BF-BOF route and 2.5 t CO_2/t crude steel for coal-based directly reduced iron (DRI) processes (Carpenter 2012). Those generation figures are minimum which can be achieved; however, there are several steel plants which are operated at higher rate of generation of CO_2.

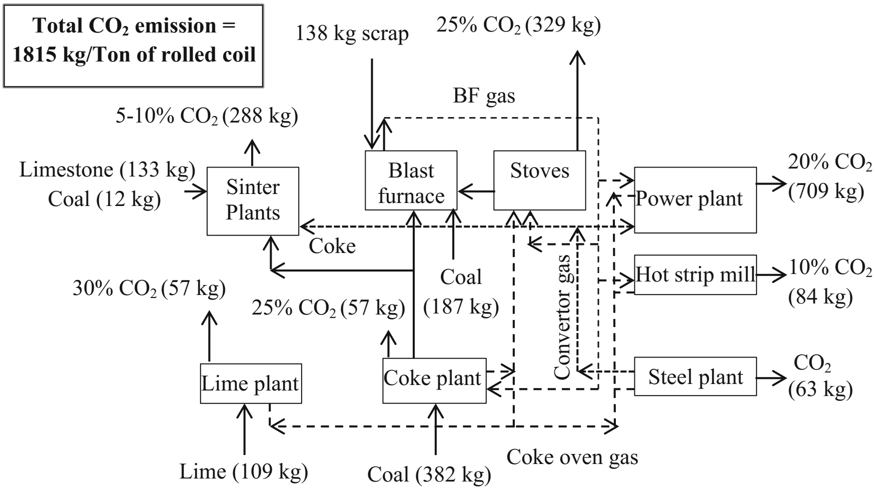


Fig. 2 CO_2 emission in typical steel mill (*Source* Carpenter 2012)

2.2 *Minor Sources*

There are number of side stream processes which also contribute to CO_2 generation such as lime (CaO) production, coal to coke conversion, power generation, transportation of raw materials and finished product, mining, etc. Intergraded steel plant, being a minor source lime plant, is identified as the maximum contributor of CO_2, where 56 kg of lime production results in 44 kg CO_2 generation. Moreover, all captive power plants are petroleum or coal based, thus those also contribute an appreciable amount of CO_2.

3 Perspective of CO_2 Emission by WSA

World Steel Association (WSA) has standard practice (ISO 14404:2013) to assess the intensity of CO_2 emission from iron and steelmaking process. WSA separated whole steel industry in two parts such as steel plant with blast furnace and steel plant with EAF (CO_2 emissions data collection). The CO_2 emission data is collected based on actual performance of any plant which is very confidential. This data helps a company to see where they stand in comparison to other steelmakers and to achieve the benchmarking CO_2 emission by a steel plant around the world. Such type of data collection includes those companies having ISO 27001 accreditation and WSA cannot disclose the individual emission data. Moreover, the collected CO_2 emission data is useful to identify opportunities for improvement. According to WSA, in the last 50 years, 60% energy consumption per tonne of steel production has been reduced by all steel industries. Several modifications have been done to recover and effective utilization of waste energies. However, WSA reported that due to huge improvement in energy consumption, there is a limited option for further improvement based on existing technology. A recent study by WSA has shown that the average energy intensity is 20 GJ/t for crude steel productions with an improvement of 15–20%. It is not necessary that the plants with low energy intensity have the most advanced equipment but they have improved their performance to limit CO_2 emission. WSA has insisted that governments should encourage steelmaking companies to establish healthy environment and to minimize steel waste by recycling waste material for sustainable growth. However, the progress in breakthrough technology development in steelmaking and implementation must be required to improve the reduction of level of CO_2 emission. WSA has also published the details of different approaches for the reduction of CO_2 from steel industries (Steel's contribution to a low carbon future).

4 Available Technologies for CO_2 Capture and Sequestration

Carbon oxide capture from flue gases can be broadly classified in four ways based on the basic principle such as absorption, adsorption, cryogenics and membrane based separation (Olajire 2010; Sarkar et al. 2014). The working range and the purity of separated CO_2 have been shown in below chart (Fig. 3). Those four methods can be carried out in several ways as illustrated below.

Absorption of CO_2 is mainly two types, i.e. chemical absorption, which is carried out using different types of amines, aqueous ammonia and alkaline solution and whereas physical absorption is done with help of Selexol process, Rectisol Process, Fluro Process and NMP-Purisol Process. Adsorption of CO_2 can be done using different types of porous materials such as alumina, zeolite, activated carbon, etc. Regeneration adsorption methods are pressure swing, temperature swing and electrical swing. In membrane-based separation processes different types of polymeric and ceramic membranes are used for CO_2 separation (Olajire 2010).

Different processes for post-combustion CO_2 capture are being developed but very few are at the doorstep of commercialization. Among all methods, solvent-based chemical absorption of CO_2 is most feasible technology for commercial implementation in near future (Steeneveldt et al. 2006). Furthermore, it is

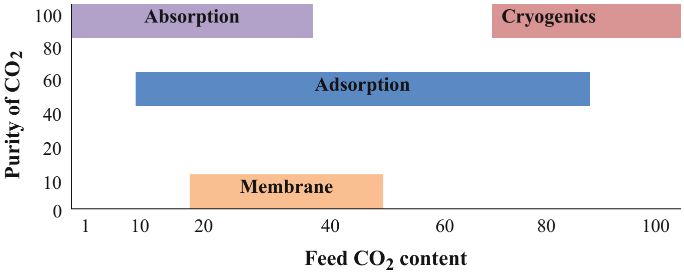


Fig. 3 Different types of CO_2 capture technologies and their working range

not only important to separate CO_2 from flue gases but also it is important to store or sequester CO_2 for long term. In current scenario, geological sequestration of CO_2 is highly encouraging. Based on the available literatures, different carbon dioxide emitting industries have taken initiatives to reduce CO_2 emission to conserve, protect and improve healthy environment. Hence, such type of developments by steel industries is described in next section.

5 Progress of Carbon Capture and Sequestration (CCS)

Worldwide steel plants have taken initiative to lower down their CO_2 emissions either by capturing CO_2, which is coming out from the process, or by developing new process technology for the reduction in CO_2 generation. The oldest and most efficient technique of CO_2 capture can be carried out by physical or chemical absorption process using aqueous ammonia or different type of ammine. Several companies have adopted this approach though it has not been implemented in full scale due to some process intricacy. Initiatives have also been taken to reduce the overall power consumption inside the plant and coke rate to the blast furnace so that the level of CO_2 generation reduces to a certain extent.

5.1 Ultra-Low Carbon Dioxide (CO_2) Steelmaking (ULCOS)

Very recently, a group of companies have taken an initiative to reduce CO_2 emission during steelmaking, which is called ULCOS, stands for Ultra-Low Carbon dioxide (CO_2) Steelmaking (ULCOS) (Birat et al. 2009; Birat and Lorrain 2009, Birat 2011; Van der Stel et al. 2011, 2014). As the development of such process is very challenging task, a consortium has been formed to carry out different experiment and to nullify different challenges. Moreover, development requires a huge investment. The consortium consists of different types of 48 companies and organizations from 15 European countries. They have launched a cooperative research and development initiative to enable drastic reduction in CO_2 emissions from steel production. The association consists of all major EU steel companies, energy and engineering partners, research institutes and universities and is supported by the European commission. The aim of the ULCOS programme is to reduce CO_2 emissions of today's best routes by at least 50%. Four major processes have been proposed under ULCOS initiative such as ULCOS-BF and several experiments have been conducted so far as described below. Under this, process pressure swing adsorption (PSA) method has been adopted to separate out CO_2.

5.1.1 Top Gas Recycling Blast Furnace with CCS

The concept of the top gas recycling blast furnace is very simple but hard to implement which has been schematically represented in Fig. 4. In this process, the

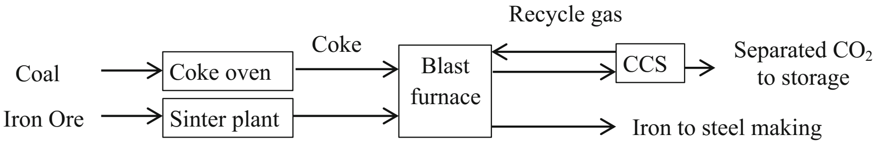


Fig. 4 Schematic representation of top gas recycling blast furnace with CCS

useful components of the gas can be separated out by capturing and storing of CO_2 and separated gas is recycled back into the furnace to reuse as a reducing agent. Moreover, during the process, pure oxygen is supplied into the blast furnace instead of air so that the availability of nitrogen reduces inside the system. Thus, this concept not only separate out CO_2 but also reduce the rate consumption of coke in blast furnace. In 2007, a gas separation plant was constructed and the experiment has been successfully conducted in LKAB's experimental blast furnace in Luleå, Sweden (Birat 2011) to establish the present concept. Very soon, the trial will be conducted on commercial scale. In this process, up to 94% CO_2 has been captured so far with the help of PSA and separated CO_2 is stored in underground reservoir.

5.1.2 HIsarna Smelter Technology

The concept of HIsarna is based on bath-smelting. In this process, coal is directly fed to the blast furnace after preheating and partial pyrolysis and ore is injected after melting in melting cyclone. The final iron production takes place in smelter vessel. This method significantly reduces coal usage which implies less generation of CO_2 (Fig. 5). CCS method is also associated with this novel process and separated gas can be used for electrical energy generation. Moreover, in this method coal can be partially replaced by biomass, natural gas or even hydrogen. The pilot scale has been successfully completed in 2010 and now before going to industrial scale, semi-industrial scale is required to verify the feasibility of the process (Birat 2011).

5.1.3 ULCORED

In ULCORED method natural gas is used as a reducing agent and iron is produced in solid state (Birat 2011) and the principle of this process is based on DRI method as shown in Fig. 6. Thus, for steelmaking process EAF is required. This process is

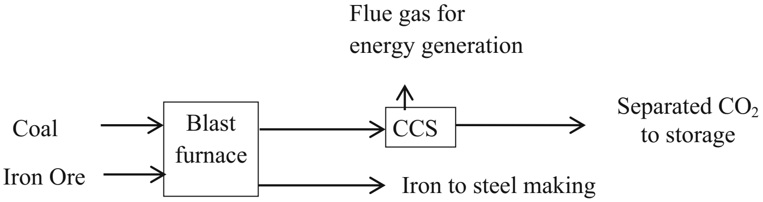


Fig. 5 Schematic representation of HIsarna smelter technology with CCS

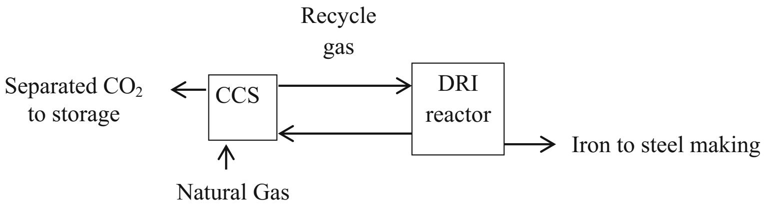


Fig. 6 Schematic representation of ULCORED DRI technology with CCS

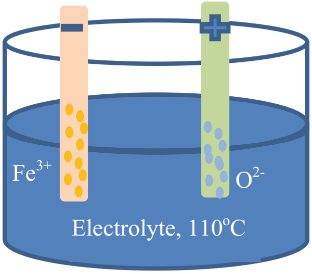
costly and has some limitations such as better quality iron ore is required, huge electric consumption, etc. Under ULCOS, this is the only initiative for direct reduction of iron ore however, revalidation of this process is very essential to make it feasible for reduction of iron ore.

5.1.4 Alkaline Electrolysis

The basis of this method is electrolysis of iron ore which is the least developed process route currently being studied in ULCOS. This process would allow the transformation of iron ore into metal and gaseous O_2 using only electrical energy. Adaptation of this process will eliminate the conventional coke ovens and blast furnaces for iron production. In current practice, metals like aluminium, zinc, and nickel are produced via electrolysis method however, till date no such industry is available where iron is produced by this method. Two type of electrolysis methods have been tested so far, i.e. Ultra-Low Carbon dioxide Electrowinning (ULCOWIN) and Ultra-Low Carbon dioxide Electrolysis (ULCOLYSIS) (Birat 2011).

The ULCOWIN process (Fig. 7) is based on principle of electro winning and can be carried out at a temperature of 110 °C, and whereas ULCOLYSIS is carried out at a temperature of 1600 °C. The successful trail has been conducted for both technologies in lab scale and further research is going on to establish these process in larger scale. In both cases, the anode is made of an inert material which does not react with oxide mixture. Pure oxygen evolves as a gas at the anode and iron is produced as a liquid metal at the cathode. Among these two categories, ULCOWIN is at a more advanced stage (4 kg/day) of development than ULCOLYSIS.

Fig. 7 Schematic representation of ultra-low carbon dioxide electro winning (ULCOWIN) technology



A rigorous research work is essential to establish alkaline electrolysis method for production of iron without generation of CO_2.

5.2 *Adsorption-Based CO_2 Capture*

The absorption of CO_2 using alkaline solution and amines is very common and well established method for last few decades. However, commercialization of such process is very challenging in deed. Some major developments have been made by different industries which have been discussed below.

5.2.1 Aqueous Ammonia Based CO_2 Capture

POSCO and RIST of South Korea jointly investigated the removal of CO_2 from blast furnace gas using aqueous solution of ammonia (<10 wt%) (Rhee et al. 2011; Ahn et al. 2011). The principle of the process is simply based on chemical absorption. Consequently CO_2 is absorbed using aqueous NH_3 solution in absorber and NH_3 is regenerated in stripper as shown in Fig. 8. According to report first stage pilot plant having capacity of 50 Nm^3-BFG/h has been completed on 2008 (Rhee et al. 2011) and in second stage pilot plant with capacity of 1000 Nm^3-BFG/h has been successfully conducted on late 2011 (Ahn et al. 2011). In both the cases, the recovery of CO_2 was more than 90% and the purity of CO_2 was more than 95%. The energy consumption is very low for this ammonia-based process (2.0 GJ/tonne-CO_2). Moreover, it has been also estimated that this process is more effective than chilled ammonia process for capturing of CO_2, developed by ALSTOM and American Electric Power (Ahn et al. 2011). Based on pilot scale study, it is expected that this developed technology will be deployed in POSCO steel industries to reduce the CO_2 emission from blast furnace in very near future.

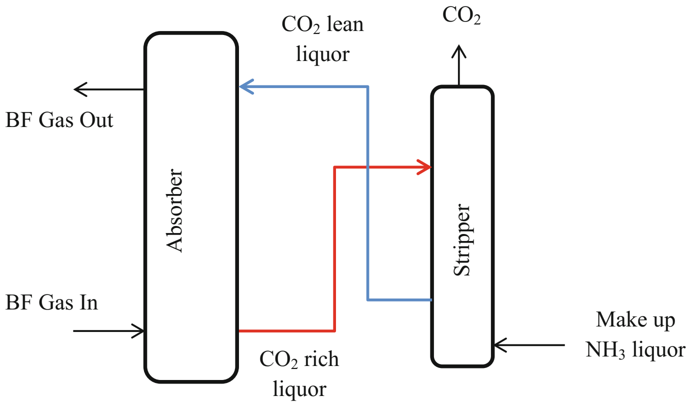


Fig. 8 Schematic representation of CO_2 separation using aqueous ammonia

5.2.2 Amine Based CO_2 Capture

In recent years, amine-based CO_2 capture process earns special attention due to favourable reversible reactions with CO_2, which ease the operation for the regeneration of amines as well as the separation of CO_2 from many CO_2-containing gases, including flue gas (Dutcher et al. 2015; Dave et al. 2008). The main challenge of this technology is the identification of proper amine or mixed of amines as capturing solution and different initiatives have been taken by steel industries to address this.

6 Global CCS Project in Steel Industry

In last decade, Steel industries and Government of Japan have been introduced a CCS project named as COURSE 50 with collaboration of New Energy and Industrial Technology Development (NEDO) (Watakabe 2013). Under this programme two objectives have been considered; first one is the reduction CO_2 generation and second aim is capture and utilization of CO_2. In the first initiative, the reforming of coke oven gas (COG) has been considered to increase hydrogen content (from 55 to 67%) and after reforming COG could be utilized as reducing agent in blast furnace to ensure the reduction in CO_2 generation. A novel amine-based absorber development is the major objective to capture CO_2. Using the novel amine compounds, two stage pilot scale study has been successfully completed under COURSE 50. The main principle of this method is very similar as described in Fig. 8. In first stage (CAT1), the capacity of pilot plant was 1 tonne CO_2/day and after successful completion of that pilot plant, 30 tonne CO_2/day capacity pilot (CAT30) was commissioned successfully. It is expected that in near future, such developed technology will be deployed in other steel industries of Japan.

Most promising development for field application of CCS has been done so far by Emirates Steel Industries (ESI) along with Abu Dhabi National Oil Company (ADNOC) and Abu Dhabi Future Energy Company, Masdar. In 2006, Masdar initiated CCS project and in between 2009 and 2011, the pilot scale with capacity of 60 tonne/day CO_2 injection was completed. The actual field application has been started in the year of 2013 with the help of Dodsal Engineering and Construction Group. In this process, CO_2 is captured from DRI iron making process using amine-based separation process and separated CO_2 is dehydrated and compressed for transportation at site location of ESI. Compressed CO_2 is transported via pipe line of 47 km to ADNOC for utilization in enhanced oil recovery (Abu Dhabi CCS Project). The target of this project is to capture 0.8 Million tonnes per year.

7 Reduction of Indirect Emission

Energy requirement is directly related to CO_2 emission for fossils fuel based industries and steel industries are among them. Therefore, reduction in energy consumption results in decrement of CO_2 emission. All steel plants would lower their indirect CO_2 emissions (that is, emissions from the consumption of electricity produced off-site) if they could switch to electricity generated from hydroelectric or nuclear power plants, or from renewable energy. If this were possible, it could result in near-zero CO_2 emissions for a scrap/EAF mini-mill. In the future, indirect CO_2 emissions from the iron and steel industry will gradually decrease due to decarbonisation of electricity. Very recently the utilization of solar energy as well as use of energy efficient equipment have been tried to reduce the overall power consumption. Moreover, replacement of vapour lamps with LED light is effective way for the reduction of indirect consumption of energy as well as CO_2 emission. Waste heat recovery is major area where steel industries can involve themselves to reduce the overall energy consumption.

8 Conclusions

Steel industries are very keen to establish technologies for CCS. As per earlier discussion, it is very satisfactory that after successful pilot scale study we are at door step for commercialization of different methods. However, several methods require huge development for industrial application. Government of several countries becomes more stringent about the level of GHG emission. Hence, steel industries are bound to reduce the level of CO_2 emission. However, as CO_2 emission has become major concern for the human race, CCS technology is a lucrative area of research for both academics and people from industries.

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Chapter 18
Carbon Emissions and Their Mitigation in the Cement Sector

Shashank Bishnoi

Abstract Cement is a ubiquitous building material in the developing and the developed world due to its flexibility of production and use. Despite being a relatively sustainable material, the large quantities of cement produced make it one of the biggest contributors to CO_2 emissions. The cement industry has been tackling this issue through the improvement of production technologies and higher replacements using supplementary cementitious materials. New cements that have lower specific emissions and those that consume CO_2 are also being developed. Still, the projections of the growth of the cement industry indicate that carbon capture and storage will be important for meeting the emission reduction targets set by the industry.

Keywords Cement industry · CO_2 sequestration · Alternate technology · Cement curing

Abbreviations

IBEF	India brand equity foundation
OPC	Ordinary portland cement
PPC	Portland pozzolanic cement
PSC	Portland slag cement
LCCC	Limestone calcined clay cement
CSI	Cement sustainability initiative
SCM	Supplementary cementitious material
CMA	Cement manufacturers association
WBCSD	World business council for sustainable development

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1 Introduction

Construction is considered to be an essential activity for the development of any country and concrete is the most widely used construction material. It is also the largest man-made material in the world. Concrete is generally a low cost and low embodied energy material since it is made of locally available natural materials like crushed rocks and sand. It is the cement that binds these components together that is energy intensive, has high CO_2 emissions and is therefore considered to not be environmentally friendly.

Despite being less than 20% of the weight of concrete, cement production contributes to nearly 7% of global anthropogenic CO_2 emissions. This is due to the large volumes of cement produced around the world. India alone produced more than 270 million tonnes of cement in the year 2015 (IBEF 2016). Each tonne of cement produced is associated with approximately 0.65 tonnes of CO_2 emitted to the atmosphere (Gartner 2004). Although these values appear to be high, it must be noted that most of the other alternatives to cement and concrete are relatively more energy and emission intensive. This means that replacing cement and concrete with other materials would not lead to a reduction in CO_2 emissions, as will be discussed later (Juenger et al. 2011). This paper discusses the sources of CO_2 emissions in cement production, various alternatives that reduce these emissions and the consumption of CO_2 in cements.

2 Source of CO_2 Emissions

There are two main sources of CO_2 emissions in cement production. The first source is the decomposition of carbonate rocks at a high temperature and the second is the combustion of fossil and other organic fuels required for achieving these high temperatures. Both these sources are discussed in this section.

Portland cement is mainly composed of combined oxides of calcium, silicon, aluminium and iron, of which calcium makes the largest fraction. Limestone, which is an impure form of calcium carbonate, is the most common source of calcium in cement. Being a naturally occurring stable material, calcium carbonate has to be calcined to calcium oxide in order to achieve cementitious properties. The reaction occurring during the calcination of calcium carbonate is shown in Eq. 1. The numbers below the equation represent the molecular mass of the reactant and the products, showing that approximately 44% of the weight of calcium carbonate is lost in CO_2 that is emitted to the atmosphere. This CO_2 is referred to as mineral CO_2 (MCO_2).

$$\begin{array}{ccc} \mathrm{CaCO_3} & \rightarrow & \mathrm{CaO} + \mathrm{CO_2} \\ (100) & (56) & (44) \end{array} \tag{1}$$

The decomposition as above takes place at temperatures below 850 °C in rotary kilns. At higher temperatures up to 1450 °C, this calcium oxide combines with other oxides to form calcium silicate and calcium aluminate phases. The fired material usually comes out of the rotary kiln in the form of a few centimetres large nodules known as clinker. Clinker is generally ground with gypsum, which is an impure form of hydrated calcium sulphate, to produce Ordinary Portland Cement (OPC). Since most Indian OPCs contain 58–64% calcium oxide (Kaur 2016), approximately, 450–510 kg of MCO_2 is emitted from the production of every tonne of OPC (Gartner 2004).

Additionally, approximately 3 GJ of energy is consumed from fossil fuels per tonne of clinker to bring the raw materials to the high temperatures required for clinkerisation (Gartner 2004). The CO_2 emitted from the combustion of the fuels is known as the fuel CO_2. Depending on the source of this energy, a total of approximately 1 tonne of CO_2 as a combination of mineral and fuel CO_2 is emitted for every tonne of clinker produced.

3 Emission Reduction Strategies

The cement industry has taken significant steps to reduce CO_2 emissions and energy consumption, especially since the 1990s (Gartner 2004). Most cement plants employ technologies like multi-stage preheaters and precalciners, improved cooling technologies and waste heat recovery systems to achieve high energy efficiencies. Additionally, the increased usage of alternative fuels, such as municipal solid waste and used tires have reduced the CO_2 emissions attributed to cement production.

Significant efforts have also been made on the side of the materials as well and blended cements have become common with the average clinker factor, i.e. the gravimetric proportion of clinker per unit weight of cement, in most developed countries is of the order of 0.70 (CSI 2009).

The strategies used by the industry to achieve a reduction in the specific emissions of cements are discussed in this section.

3.1 Blended and Special Cements

Currently, OPC only makes around 25% of the Indian cement market, while most of the cements available are blended cements containing supplementary cementitious materials (SCMs) like fly ash and slag. Cement containing fly ash is known as Portland Pozzolanic Cement (PPC) and cement containing ground granulated blast-furnace slag is known as Portland Slag Cement (PSC). Since PPC can contain up to 35% of fly ash and PSC can contain up to 70% of slag, CO_2 emissions from their production are lower than those from OPC due to the lower clinker content in these cements. PPC and PSC also perform better than OPC on several fronts, especially with respect to durability of concrete. For these reasons, policies to encourage their use exist around the world. Additionally, since the SCMs are

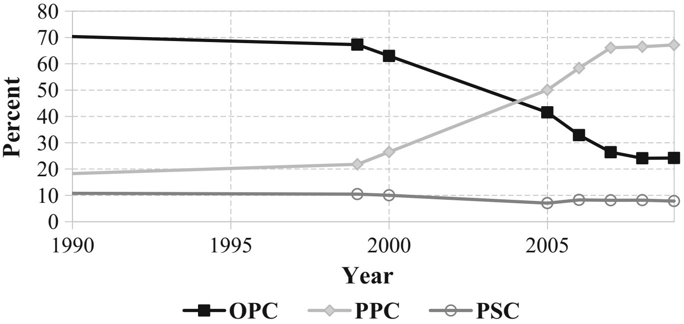

Fig. 1 Proportion of cement types produced in India since 1990 (CMA 2012)

generally available at relatively lower costs than clinker, their use in cements is commercially attractive.

In India and China, the two largest producers of cement, most of the cement produced is already blended with fly ash, while in many cases fly ash is mixed in the concrete on site. In the case of United States, the third largest producer of cement, although most of the cement produced is OPC, fly ash is blended in concretes at the site or in ready-mix concrete plants, which supply concrete to sites in trucks. This makes fly ash the largest SCM used around the world. Still a majority of fly ash produced today is not gainfully utilised. This is because the addition of much larger quantities of fly ash to cement leads to a loss in performance of concrete. The growing demand for power in developing countries implies that even more fly ash is expected to be available in the future. However, since the demand for cement is expected to grow at a slower pace, it is expected that the unused quantity of fly ash will continue to increase in the near future.

Although fly ash has been known to be an effective partial replacement of clinker for almost a century, its widespread use in construction in India started in 1990s. Figure 1 shows that the proportion of PPC in the Indian market started to increase significantly since the 1990s. The sudden shift was due to a change in policy that made it easier to handle fly ash for use in cements.

Ground granulated blast-furnace slag, or slag in short, has been permitted as a partial replacement of clinker in several national standards for over a century. Due to their higher calcium contents and their slightly hydraulic nature, slags can replace more of clinker than fly ash and most standards, including the Indian ones, allow a replacement of up to 70% of clinker by slag. However, since the quantities of steel produced are much lower than the quantities of cement produced, the availability of sufficient quantities of slag is generally limited to areas near active iron mines.

Other by-products such as rice husk ash from agriculture and silica fume from the silicon industry are also used as SCMs. However, various factors such as their low quantities and the lack of logistics affect their wider use.

Some naturally available materials such as limestone, stone cutting dust and reactive clays have also been used as SCMs. European cements allow up to 30% of clinker to be replaced by crushed limestone and most OPCs around the world can contain up to 5% of crushed limestone as a performance improver. Since these materials are naturally available and require little to no processing, they reduce the CO_2 intensity of cements.

Industrially produced SCMs such as metakaolin and calcined shales are also being used in the industry. Since these materials require much less processing than clinker and can replace more than their own weight of clinker, they can prove to be environmentally friendly replacements. However, some performance issues with these materials and the large availability of fly ash have prevented their increased usage.

Due to the limitations discussed above, it is difficult to reduce the average fraction of clinker in cements to values lower than 70% using the above supplementary cementitious materials individually. Ternary cements, sometimes also known as composite cements, that utilise the synergy between two or more SCMs, can help in further reducing the clinker factor, and therefore CO_2 emissions from the production of cements. However, the relatively more complicated behaviour of these cements, and the lack of experience in their use, prevents their widespread use. For example, the standards in many countries, including India, allow the production of composite cements containing a combination of fly ash and slag as clinker replacement. While the slag allows lower clinker factors, fly ash overcomes some performance issues such as slower strength development and higher permeability related to slag. However, due to the limited availability of slag, the availability of this cement is likely to be limited to areas with an active production of iron.

Limestone Calcined Clay cement, or LC^3 in short (LCCC 2016; Emmanuel et al. 2016), is another composite cement which achieves a performance similar to OPC at clinker factors as low as 50–40%. This cement is a blend of clinker, calcined clay, limestone and gypsum. While no calcination is needed for the additional limestone, the clays are calcined at much lower temperatures in the range of 800 ° C, leading to up to 30% reduction in CO_2 emissions and 20% reduction in energy consumption. Due to the large potential in reducing the environmental impact of cement production, a significant thrust in the development of LC^3 is currently being made worldwide with a special focus on Cuba and India. A large research programme to understand the performance of LC^3 in the laboratory and in real structures is currently underway. Several structures have already been constructed using this cement both in Cuba and in India.

Aether (2016), a technology patented by Lafarge, is another industrially interesting approach to producing low CO_2 cement. Aether utilises the synergy of hydration of calcium sulfoaluminate (ye'elemite) and dicalcium silicate (belite) phases. While the ye'elemite phases exhibit rapid reactions giving early strength development to the cement, belite reacts more slowly contributing to long-term strength development. Aether contains lower amounts of calcium and is produced at lower temperatures (1225–1300 °C), leading to up to 30% reduction in CO_2 emissions. The performance of both LC^3 and Aether concretes have been reported to be similar in most aspects and these cements are expected to play an important role in improving the sustainability of cement production in the near future.

Geopolymers are another class of cements where aluminosilicates, mostly slag, calcined clays and fly ashes, are mixed with strong alkalis, leading to reactions where long chain products are formed (Davidovits and Davidovics 1991). These cements are generally clinker free since caustic solutions of sodium silicates are used as alkalis. Geopolymer concretes generally require curing at temperatures as high as 80 °C, as opposed to the ambient conditions required for normal concrete, and are known to develop strength at slightly slower rates than OPC at these temperatures. Still, the long-term performance of geopolymers has been shown to be satisfactory. Although some researchers have called geopolymers as low-CO_2 cements, they have been criticised by others since the production of the alkalis required for these cements has a significant environmental footprint. Moreover, the higher temperatures generally required for their curing makes this cement more suitable for the precast concrete industry and more difficult to use for general construction.

The use of most of the above approaches requires the availability of carbon neutral industrial by-products such as fly ash, slag and silica fume. The entire CO_2 emissions from the processes that produce these materials are generally attributed to the main product such as electricity for fly ash and iron for slag. It has, however, been argued that since both fly ash and slag are now considered to be important resources and not just waste materials, a part of the emissions from the parent processes should also be attributed to them. It is expected that while that such changes in accounting may impact the CO_2 intensity of the cement industry, the benefits from the reduced production of clinker and the utilisation of these by-products to an overall reduction of global warming will continue.

3.2 Calcination and Grinding Technologies

Calcination technologies have seen tremendous advances during the last several decades with the development of highly efficient systems. Older cement plants used a wet process, where the raw materials were blended together in water making the process simpler. A large amount of energy was required to dry the raw materials before cement could be produced. Cement plants today have transformed from being relatively simple kilns to complex equipment, where each step of the process is highly optimised to achieve high energy efficiency. Most of the modern cement plants use more sophisticated dry process equipment in which all raw materials are ground and blended in a dry state. Preheaters and precalciners are used to reduce the consumption of fuel required for calcination. Preheaters are cyclones where powdered raw materials get heated before entering the kiln, using the heat contained in the gases coming from the rotary kiln. In many cases, precalcination of calcium carbonate to calcium oxide is carried out by raising the temperature of the raw materials up to 900 °C even before the material enters the kiln. This reduces the total fuel and energy required for the production of clinker. Generally preheaters are mounted in several stages providing incremental heating to the raw materials. Since preheaters reduce the residence time required in the rotary kiln, they also increase the productivity of cement plants. The reduction in fuel costs and the increased productivity, both contribute to increasing the commercial viability of preheaters. These improvements in calcination technologies are considered to have lead to a reduction in fuel energy requirement for the production of clinker by as much as 40% (Gartner 2004).

Ball mills are most commonly used for the grinding of cement. These mills contain a series of rotating cylindrical chambers where clinker and additives are ground together using high-strength steel balls and cylinders. More efficient technologies that use vertical rollers or roller presses, through generally more expensive to instal, can reduce the electrical consumption in grinding by as much as 25% (CSI 2012). Ball mills are also known to be more noisy. For these reasons, most of the new cement plants have started to prefer vertical roller mills compared to traditional ball mills.

3.3 Cooling and Waste Heat Recovery Systems

Many cement plants also use coolers and waste heat recovery systems that use the residual heat in the clinker and the waste gases to generate electricity for use in the plant. It has been estimated that almost 40% of the input energy in a modern dry process cement kiln remains in the exhaust gases, which have temperatures as high as 400 °C, and the clinker produced in the kiln, which has temperatures as high as 300 °C. It has become common to divert this heat to boilers and turbines to co-generate electricity for use in the cement plant. In modern cement plants having waste heat recovery systems, the temperature of the final exhaust gases can be as low as 70 °C. Still, the high cost of installation of these systems and the relatively low efficiency of extraction of energy at these temperatures can be a barrier to the adoption of this technology.

3.4 Alternative Fuels

The use of alternative fuels in cement plants offers two-fold advantages. First, it allows the gainful utilisation of waste materials like municipal solid wastes. Second, since the decomposition or incineration of the wastes would have led to the evolution of greenhouse gases, additional emissions from the production of clinker are avoided. For this reason, the CO_2 emitted from the burning of alternative fuels is generally accounted for in the process that produced the waste and not in the production of clinker. In many countries like Japan and Switzerland, alternative fuels account for the majority of energy consumed in a cement kiln. In India, they currently account for less than 1% of the energy consumed in the cement industry. Segregation of wastes, logistics and policies allowing their movement and the calorific value of alternative fuels are some of the most important challenges that affect their usage (CMA 2015).

While the strategies discussed above are used to reduce CO_2 emissions from cement production, the sections below discuss the consumption of CO_2 in cements.

4 Consumption of CO_2 in Cements

4.1 Carbon Sequestration in Portland Cements

Cement provides binding in concrete by reacting with water and producing hydrated phases that fill the microstructure of concrete and reduce its porosity. An example hydration reaction is shown in Eq. 2.

$$(CaO)_3 . SiO_2 + 5.3H_2O \rightarrow 1.3Ca(OH)_2 + (CaO)_{1.7} . SiO_2 . 4H_2O \tag{2}$$

After these reactions, concrete still contains a network of fine connected pores through which gases and liquids can flow. In a process called carbonation, most of the hydration products of cement react with CO_2 in the air that enters the concrete through this pore network. Examples of the carbonation reactions of the hydration products in Eq. 2 above are shown in Eqs. 3 and 4.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{3}$$

$$(CaO)_{1.7} . SiO_2 . 4H_2O + 1.7CO_2 \rightarrow 1.7CaCO_3 + SiO_2 . 4H_2O \tag{4}$$

Through similar reactions, most of the calcium in the hydration products is eventually converted back to $CaCO_3$ if it is allowed to come in contact with CO_2. Carbonation can reduce the durability of reinforced concrete structures by reducing the alkalinity of the water in the pores of concrete, thereby increasing the risk of corrosion of reinforcing steel. However, the process of carbonation is observed to be self-limiting in structures and it generally only affects the first few centimetres of concrete.

Due to this, during the life of a structure, the total CO_2 consumed in carbonation is insignificant. In the long-term, the demolition and crushing of concrete would allow most of the mineral CO_2 released from the decomposition of $CaCO_3$ to be reabsorbed in concrete. However, concrete cannot reabsorb the fuel CO_2 emitted from the combustion of fuels during the production of cement. It must be noted that blended cements can consume less amount of CO_2 through carbonation since they also produce less mineral CO_2 than OPCs during their production. Furthermore, pozzolanic materials convert calcium hydroxide to calcium silicate hydrate, which carbonates more slowly than the former. It is still be beneficial to use blended cements as they contain lower quantities of the energy-intensive clinker and have been found to be more durable, increasing service life and reducing the need for repair of structures.

4.2 Cements that Consume CO_2

Some new cements that consume CO_2 have also been developed. One such technology is Solidia, which is supported by Lafarge (Solidia 2016). In Solidia, CO_2 emitted during the production of cement and other materials is captured, stored and pumped into precast concrete. Solidia cement contains a monocalcium silicate phase, which contains significantly lower quantity of calcium and can be produced at lower temperatures than ordinary clinker, thereby producing lower CO_2. This special cement hardens by absorbing CO_2 in the presence of water, converting calcium silicate to calcium carbonate and silica gel. Solidia concrete has been shown to possess similar performance as normal concrete in precast applications.

Calera Corporation is promoting another patented technology that utilises carbon sequestration to convert CO_2 into a building material (Calera 2016). In this technology, captured CO_2 is pumped into an alkaline aqueous solution containing calcium salts to convert them into calcium carbonate. The calcium carbonate produced can be spray-dried for use as a partial replacement of clinker phases in cement or as aggregates. It is envisaged that industrial waste streams or sea water will be used as the aqueous solution for the production in the future. It has also been claimed that this calcium carbonate can be used as a cementing material by blending with other proprietary chemicals that convert $CaCO_3$ from the particulate vaterite phase to an interconnected network of aragonite phase, leading to a hardening of the paste. However, the commercial and environmental benefits of this phase conversion reaction have been questioned due to the potentially large environmental footprint of the chemicals used in this process.

Another technology known as CO_2NCRETE, which combines captured CO_2 with lime to produce calcium carbonate using a 3D printing technology has been reported recently. It must be noted that lime is generally produced through decomposition of calcium carbonate at high temperatures, which involves large amounts of mineral (as shown earlier in Eq. 1) and fuel CO_2 emissions. Since the maximum amount of CO_2 sequestered in this process cannot be more than the mineral CO_2 released from the decomposition of calcium carbonate and there being additional fuel CO_2 released from the combustion of fuels, the claim of this process being overall carbon negative appears to be inaccurate. Furthermore, the additional benefits of mixing lime with CO_2 over its use as a binder in combination with pozzolanic materials is also not clear. Both, Solidia and Calera, are currently limited to the laboratory and field applications of the cements are not known.

5 Requirement for Carbon Capture in Cement Production

The Cement Sustainability Initiative (CSI), which is an effort of the World Business Council for Sustainable Development (WBCSD) and has many cement companies worldwide as members, has released emission reduction targets, planned to be achieved by the year 2050. After considering the potential of all the technologies considered above, CSI has estimated that almost 56% of emission reduction would have to be achieved through carbon capture and storage (CCS) in order to achieve the targets.

CCS is so far an unproven technology in the cement industry, primarily due to the high costs involved. Post-combustion and oxy-fuel technologies have both been identified to be potentially interesting for application to the cement industry. In the post-combustion technology, the CO_2 emitted from the kiln could be captured using physical or chemical adsorption processes and stored in a stabilised form. In the oxy-fuel technology, combustion is carried out in a pure stream of oxygen, yielding a relatively pure stream of CO_2 that would be more feasible to capture. Trials have been carried out where the CO_2 produced from cement plants have been used to grow micro-algae using photosynthesis. Algae such as Spirulina, which is a dietary supplement identified useful for malnourished children by the World Health Organisation, can also be produced in such processes.

The commercial viability of CCS has been seen to be limited in the near future. Still, due to the lack of other alternatives, CCS is still considered to be an important option to pursue in order to achieve the emission reduction targets set by the cement industry.

6 Avoided Emissions from Use of Cement

Apart from estimating the CO_2 emissions from the production of cement, the emissions avoided due to the use of cement can also be used to assess its sustainability. Avoided emissions can be defined as the additional emissions that would have taken place through the use of an alternative materials or technologies if the use of cement had not been possible. It must first be noted that due to the local nature and abundant availability of the raw materials used in the production of cement and concrete, few alternative materials can be produced in the large quantities in which cement and concrete are produced. Additionally, in many applications, alternatives to concrete are not available. So, such a calculation is only theoretical in nature as no alternative for a 100% replacement of these materials is currently available.

Assuming that 1 m^3 of normal concrete, having a weight of approximately 2300 kg, contains around 375 kg of cement, the associated CO_2 emissions can be estimated to be around 120 kg of CO_2 per tonne of concrete. Due to the higher strength to weight ratio of steel, it can be assumed that the weight of steel required in a structure will be 30–50% of the weight of concrete required for the same structure. Since more than 1 tonne of CO_2 is emitted per tonne of steel produced, the CO_2 emissions would be as much as 2–4 times higher if the same structure were to be built using steel. Much higher figures can be calculated for clay bricks, where the entire material has to be fired at a high temperature to achieve strengths less than half to a third of normal concrete.

Natural materials such as bamboo and timber have also been promoted as environmentally friendly construction materials. However, it is often ignored that the replacement of concrete by these materials would lead to massive deforestation and adds pressure on the production of food. Additionally, these materials are labour intensive and also not free of processing, requiring treatments such as seasoning in steam rooms and transportation through long distances.

It can be seen from the above that, despite the relatively high contribution of cement to CO_2 emissions, more environmentally friendly alternatives to concrete are currently not available.

7 Perspectives for the Future

Given the growth expected in the developing countries, the demand for cement is likely to continue to grow to 4 billion tonnes per annum by 2050. At the current emission averages, this would mean over 3 billion tonnes of CO_2 emitted per year. A combination of all technologies discussed above is likely to be used to mitigate these emissions since it would be difficult to achieve reduction targets using any one of them.

The commercial viability of any technology to be used in the future is likely to be governed by four important factors, viz. the availability of resources, the availability of technology, the cost of production and the social acceptability of the product. Portland and pozzolanic cements are most likely to dominate the market, since they require raw materials such as limestone and clay, which are easily available throughout the world. The technology to produce Portland and pozzolanic cements is also widely available and well understood around the world. Additionally, since their use is well understood by the construction workforce around the world, no retraining is required. For these reasons, the use of special cements is likely to remain limited to niche or local applications, leading to little overall impact.

Still, given that expensive CCS techniques may be required to meet up to 56% of the reduction targets, the development of new technologies will be essential to ensure that cement continues to be available at affordable prices in developing countries. LC^3, Aether and Solidia appear to be the most promising approaches to reduce reliance on CCS. Given the large amounts of investment and time required for the development of new cements and the relatively conservative nature of the construction industry, the introduction of these new technologies as mainstream products remains a challenge.

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Chapter 19

Aqueous NH_3 in CO_2 Capture from Coal-Fired Thermal Power Plant Flue Gas: N-Fertilizer Production Potential and GHG Emission Mitigation

Amitava Bandyopadhyay

Abstract Carbon dioxide (CO_2) emission from stationary point sources connected to combustion facilities using fossil fuels in addition to other industrial sources is adversely affecting the climate on earth. Thus capturing CO_2 from the combustion sources followed by its safe stabilization or storage constitutes an important target. Legion of researches have so far been undertaken to develop absorbents, adsorbents, and membranes to remove CO_2 from combustion facilities. Capturing CO_2 from the post-combustion flue gas by the chemical absorption method using aqueous ammonia (NH_3) has been given serious attention by the researchers considering the advantages of high CO_2 capture efficiency, ease of operation, and lower investment cost. Life cycle CO_2 emission analysis revealed that capturing CO_2 from the exhaust of flue gas of a coal-fired thermal power plant (TPP) using aqueous NH_3 could be a plausible option. The possible solid reaction products of aqueous NH_3 based multipollutant capture of the flue gas from the TPP targeting for CO_2 capture would be ammonium sulfate [$(NH_4)_2SO_4$], ammonium nitrate [NH_4NO_3], and ammonium bicarbonate [NH_4HCO_3]. These products have the potential to serve as N-fertilizer. In this communication, the present status of investigations on the aqueous NH_3 based CO_2 capture process is analyzed gathering information from the existing literatures. Given the tremendous scope of research in India, the current national research potential could be gainfully utilized for envisaging the CO_2 capture by aqueous NH_3 in coal-fired TPP. In this regard, multisectoral research programs could be proposed in a planned manner for making use of the available resources in the country with the coordinated approach of few important streams such as academia, thermal power, fertilizer, agriculture, environment, and climate change. Recommendations are made for development of suitable CO_2 capture technology in Indian coal-fired TPPs.

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Abbreviations

TPP	Thermal power plant
EOR	Enhanced oil recovery
FGD	Flue gas desulphurization
GHG	Green house gas
ABC	Ammonium biocarbonate
MEA	Monoethanolamine
ECBM	Enhanced coal bed methane
CAP	Chilled ammonia process
AMPD	Amino methyl propandiol
AEPD	Amino ethyl propandiol
THAM	Ttri (hydroxymethyl) amino methane
MDEA	Methyl diethanolamine
NAAQS	National ambient air quality standards
COBP	Coke oven byproduct plant
MDA	Menthanediamine

1 Introduction

Carbon dioxide (CO_2) emission from stationary point sources connected to combustion facilities using fossil fuels, in addition to other industrial sources, is adversely affecting the climate on earth. Climate change is emerging as a growing global risk that has generated public concern for the last few decades. Thus capturing CO_2 from the combustion sources followed by its safe stabilization or storage constitutes an important target. Legion of researches have so far been undertaken to develop absorbents, adsorbents, and membranes to remove CO_2 from combustion facilities.

The classical method of absorption of CO_2 in organic amines has so far been known to us for long. But this option has shown to have problems when planned for application on large scale for a coal-fired thermal power plant (TPP). Importantly, the amine-based CO_2 capture plant demands a very sophisticated gas cleaning operation prior to deal with the flue gas for CO_2 capture. Besides, solvent loss (in the form of heat stable salts) and oxidative degradation of the solvent are now known. The development of blended solvents (amines) has thus now become an intense field of research. However, the health safety related issue is becoming equally important that also is a concern.

In view of this, capturing CO_2 from the post-combustion flue gas by the chemical absorption method using aqueous ammonia (NH_3) has been given serious attention by the researchers considering the advantages of high CO_2 capture efficiency, ease of operation, and lower investment cost. Life cycle CO_2 emission analysis revealed that capturing CO_2 from the exhaust flue gas stream of a coal-fired TPP using aqueous NH_3 could be a plausible option for CO_2 capture. Furthermore, aqueous NH_3 based CO_2 capture method has the advantage of capturing multi-pollutants likely to present in the flue gas stream such as SO_2 and NO_2 in addition to CO_2. Thus the possible solid reaction products of aqueous NH_3 based multi-pollutant capture of the flue gas from the TPP targeting for CO_2 capture would be ammonium sulfate [$(NH_4)_2SO_4$], ammonium nitrate [NH_4NO_3], and ammonium bicarbonate [NH_4HCO_3] (ABC). These products have the potential to serve as N-fertilizer. In addition to the solid reaction products, the uncollected fly ash from the highly efficient electrostatic precipitator (particulate matter emission limit of 50 mg/Nm^3) could serve as micronutrients since elements present in the fly ash have shown to offer such effects. The presence of mercury (Hg) in the flue gas stream of a coal-fired TPP has also gained considerable attention in the developed nations. However, there is no sizeable data available in India that necessitates the treatment of Hg in the flue gas. In any case, Hg needs to be removed, if it is present in the flue gas prior to NH_3 absorption.

In this article, the present status of investigations on the aqueous NH_3 based CO_2 capture process is analyzed gathering information from the existing literatures. Also the fundamental studies on post-combustion CO_2 absorption by aqueous NH_3, emphasizing its efficiency taking into consideration of the multipollutant capture option is described.

Given the tremendous scope of research in India, the current national research potential could be gainfully utilized for envisaging the CO_2 capture by aqueous NH_3 in coal-fired TPP for the purpose as mentioned earlier. In this regard, multi-sectoral research programs could be proposed in a planned manner for making use of the available resources in the country with the coordinated approach of few important streams such as academia, thermal power, fertilizer, agriculture, environment, and climate change. In the Government of India these areas are covered under different Ministries, for instance, the Ministry of Human Resource and Development (HRD) for inducting the academic potentials, the Ministry of Power for utilizing the knowledge of the Power Plant Engineers, the Ministry of Chemicals and Fertilizers for extending the knowledge of ABC manufacturing plants and others, the Ministry of Agriculture for exploring the efficacy of land application of ABC and its concomitant products, and finally the Ministry of Environment, Forests and Climate Change to formulate strategy for developing a technology-based regulatory standard in the form of CO_2 capture plant for the coal-fired TPPs in India. In this chapter many other recommendations are also put forward for consideration by the Government of India on suitable CO_2 capture technology in Indian coal-fired TPPs having potential CO_2 emissions from point stationary sources. In these recommendations, capturing CO_2 from other industrial sources is also highlighted for the overall benefit of the readers.

2 Global Patent Analysis on CO_2 Absorption

Li et al. (2012) recently analyzed the patents on CO_2 capture by different methods such as absorption, adsorption, and membrane-based separation yearwise as well as countrywise. Important and interesting features are briefly highlighted here. It was reported that the number of patents on CO_2 capture solvents (in absorption), solid sorbents (in adsorption), and membranes were 1297. The approximate distributions among them were 486 patents (37.5%) for absorption (solvent), 461 patents (35.5%) for adsorption (solid sorbents), and 350 patents (27.0%) for membranes. Given wide scope in using a large number of materials as solvent or solid sorbents, more patents on solvent and solid sorbents were found. In contrast, materials investigated for use as membranes for CO_2 capture are relatively fewer. The patent survey further revealed that until 1980 only 79 patents were published and the publication of patents has been increasing significantly since 2008. For instance, the number of patents published in 2007 was 45, while in 2011 the number was raised to 189.

Three major issues could have played a major role in increased filing of patent applications in 1990s, such as the Kyoto Protocol in 1997, the Sleipner project in 1996, and the benefits of CO_2 injection for enhanced oil recovery (EOR). However, the sharp increase in filing of patent applications at an alarming rate since 2008 might be due to the global attention on the relationship between climate change and CO_2 release followed by many other enviro-economic issues. During 2006–2010, the number of patents was seen to sharply increase and that explained to be related to the agreement made. In the United Nations Conference on Environment and Development held in Rio de Janeiro, Brazil in June 1992, the industrialized countries including the United States and Japan agreed to reduce the GHG emissions by 2010 by 5.2% compared to the level in 1990. It was further reported that Japan, USA, World Intellectual Property Organization, and China are the top four countries covering about 71% of the total patents published. It is worth noticing that, the sorbent and membrane-based patents were dominated in Japan while solvent-based patents were dominated in Australia, Germany, European Patent Office, France, and United Kingdom. It is thus understandable that the solvent-based CO_2 capture or absorption is largely investigated all over the world than other methods.

3 Historic Development of CO_2 Absorption

The historic development of absorption of CO_2 from off-gases has been well documented by Bandyopadhyay (2011) in the context of CO_2 capture from the flue gas of coal-fired TPP. Briefly, the main issues are described here. The absorption and separation of CO_2 from the mixture of sulfur containing acid gases in the hydrocarbon industry had been a subject in the history of chemical engineering in the last century. The separation of CO_2 from the flue gas of TPPs was originated back in 1970s as an economic source of CO_2 mainly EOR rather than for the GHG emission reduction option. The CO_2 capture plants commercialized in the US during 1970–1980s (Kaplan 1982; Pauley et al. 1984) were monoethanolamine (MEA) based absorption. Alkanolamine is a class of compounds that includes MEA. The development of alkanolamines for absorbing acidic gases was demonstrated first by Bottoms (1930) and a patent was granted to him in 1930. The historic development of CO_2 removal from various mixed gases using aqueous amines are discussed in an organized manner by Kohl and Nielsen (1997) excluding the flue gas of TPPs. Thus this technology was developed over 85 years ago as a nonselective solvent to remove acidic gas impurities like, hydrogen sulfide (H_2S), CO_2 from refinery off-gases as well as sweetening of natural gas streams (Kohl and Nielsen 1997). In this technology, about 75–90% of the CO_2 is removed producing a nearly pure CO_2 (>99%) in the product stream.

In an amine-based CO_2 capture plant, the flue gas is contacted countercurrently with the amine solution (MEA), in a packed absorption tower. The main reactions occurring in the absorption tower may be represented (Kohl and Nielsen 1997) by ionization of water (Eq. 1), hydrolysis followed by ionization of dissolved CO_2 (Eq. 2), protonation of alkanolamine (Eq. 3), and carbamate formation (Eq. 4) as given below:

$$H_2O = H^+ + OH^- \tag{1}$$

$$CO_2 + H_2O = HCO_3{}^- + H^+ \tag{2}$$

$$RNH_2 + H^+ = RNH_3{}^+ \tag{3}$$

$$RNH_2 + CO_2 = RNHCOO^- + H^+ \tag{4}$$

The flue gas after absorber is washed to recover residual MEA, if any, and exhausted to the atmosphere. The CO_2-rich solvent is passed through a stripper tower in which a countercurrent steam stripped off CO_2 from the amine (e.g., MEA) producing a stream of H_2O and CO_2. The H_2O is condensed out leaving a stream of CO_2 (purity >99%) that is ready for compression. The CO_2-lean solvent on the other hand is cooled in a condenser and recycled back to the absorber.

Another class of solvents known as the sterically hindered amines has reported in the literature (Goldstein, 1983; Sartori and Savage 1983; Chludzinski et al. 1986) to govern the reaction between CO_2 and amines such as AMP, 1,8-p-menthanediamine (MDA), 2-piperidine ethanol (PE). The CO_2 absorption characteristics of these amines are almost similar to those of the alkanolamines though these are not generically alkanolamines. Sterically hindered amine designed with a specific molecular configuration can have the ability for yielding independent performance based on their individual selectivity for CO_2 absorption. It was further reported from the pilot and commercial plant data that substantial savings in capital and operating cost could be achieved with the hindered amines. The solvents for commercial CO_2 absorption processes are presented in Table 1.

Apart from the amine-based absorption of CO_2, the absorption in alkali was developed since middle of the last century for studying the design parameters of gas–liquid mass transfer equipments in the discipline of chemical engineering (Lynn et al. 1955). Development of gas–liquid contacting devices in the field of mass transfer operations still finds importance to the researchers. The intrinsic mass transfer design parameters investigated are interfacial area of contact and true gas side as well as liquid side mass transfer coefficients. The absorption of CO_2 in various alkaline solutions is well documented while studies are undertaken in determining the intrinsic mass transfer design parameters over the years. Researchers have demonstrated in these studies on the uses of reactions of CO_2 with different alkaline solutions like generic amines, blended amines, hindered amines, sodium hydroxide (NaOH), and sodium carbonate/sodium bicarbonate (Na_2CO_3/$NaHCO_3$) mixture or potassium carbonate/potassium bicarbonate (K_2CO_3/$KHCO_3$) mixture (Danckwerts and Sharma 1966; Astarita 1967; Danckwerts 1970). Interestingly, the absorption of CO_2 in NaOH solution is gaining serious attention of the researchers during these days for the purpose of alkaline carbonation as a means of CO_2 capture from the waste gas streams.

Table 1 Commercial solvents for CO_2 absorption

Solvent type	Solvent	Process conditions
Physical	Rectisol [Methanol]	−10/−70 °C, >2 MPa
	Purisol [n-2-methyl-2-pyrolidone]	−20/+ 40 °C, >2 MPa
	Selexol [Dimethyl ethers of polyethyleneglycol]	−40 °C, 2–3 MPa
	Fluor solvent [Propylene carbonate]	Below ambient temperatures, 3.1–6.9 MPa
Chemical	Organic (amine-based)	
	MEA [Monoethanol amine]	40 °C, intermediate pressures
	Econamine [Diglycolamine]	80–120 °C, 6.3 MPa
	ADIP [Diisopropanolamine (DIPA) + MDEA]	35–40 °C, >0.1 MPa
	MDEA	
	Hindered amine: Flexsorb, KS-1, KS-2, KS-3	
	Inorganic	
	Potassium carbonate and catalysts; Lurgi and Catacarb processes with arsenic trioxide	70–120 °C, 2.2–7 MPa
Physical/Chemical	Sulfinol [Mixture of DIPA or MDEA, water and tetrahydrothiopene or diethylamine]	>0.5 MPa
	Amisol [Mixture of methanol and MEA, DEA, diisopropylamine or diethylamine]	5/40 °C, >1 MPa

4 Assessing the Applicability of Amine (MEA) Based CO_2 Absorption for Coal-Fired TPP

The special report of IPCC on Carbon Dioxide Capture and Storage (IPCC 2005) has systematically reviewed at length on the various methods for CO_2 capture for GHG emission reduction including CO_2 capture from the flue gas of TPPs. Besides other processes, application of amine (e.g., MEA) based CO_2 absorption process was discussed in the report. It was however, reported elsewhere in the literature (Bandyopadhyay 2011) that the amine-based CO_2 absorption was not evolved for CO_2 capture from the flue gas of TPP. In fact, the amine-based CO_2 absorption process can be adopted for the flue gas of TPP, if its quality meets the criteria of the feed gas treated in the conventional amine-based CO_2 absorption process. However, such matching of feed gas quality is seldom achieved and that necessitates the special treatment of the flue gas of TPP prior to its entry into the amine-based CO_2 absorption process.

The flue gas of a coal-fired TPP contains several contaminants, like sulfur dioxide, SO_2 = 300–3000 ppm_v, oxides of nitrogen, NO_x = 100–1000 ppm_v, and particulate matter = 1000–10,000 mg/m^3. In contrast, natural gas firing power plants generate contaminants at considerably lower levels and the concentrations here are $SO_2 < 1$ ppm_v, NO_x = 100–500 ppm_v, and particulate matter = ~ 10 mg/m^3 (Chakravarti et al. 2001). In another study (Zhao et al. 2012), the composition of the post-combustion flue gas of TPP was reported to be about 10–20% (v/v) CO_2, about 500–5000 ppm SO_2 and NO_x, and about 10–9 g/m^3 mercury. Given the effect of temperature on reaction of NO_x, the post-combustion NO_x was reported mainly as thermal NO_x comprising 90–95% (ca.) water-insoluble NO and 10–5% water-soluble NO_2. The presence of mercury includes elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate mercury (generally captured in the ESP).

The acidic gases such as SO_2 and NO_x present in the flue gas from coal and natural gas combustions, are similar to CO_2 and have chemical interactions with the amine as solvent. This is very much undesirable due to the formation of heat stable salts considering the irreversibility of the interaction and thus a loss in absorption capacity of the solvent and the risk of formation of solids in the solution. In such a situation, an extra consumption of chemicals is required for regenerating the amine with the generation of waste stream containing sodium sulfate (Na_2SO_4) and sodium nitrate (Na_2NO_3). Therefore, the removal of SO_2 and NO_x to very low levels becomes imperative before CO_2 capture. Careful attention, in addition, must also be paid to fly ash and soot present in the flue gas as these might plug the absorber in the event their concentrations are too high. It was further suggested (IEA 2007) that in order to avoid amine degradation the flue gas of the TPP for CO_2 capture would be pretreated for achieving the compositions of the contaminants prior to entry into the amine-based CO_2 absorption systems as (i) 10–30 mg/Nm^3 (or, 3.82–11.46 ppm_v) of SO_2, (ii) 40 mg/Nm^3 (or, 21.26 ppm_v) of NO_2, and (iii) <5 mg/Nm^3 of particulate matter.

Thus, the MEA-based CO_2 capture process necessitates very low SO_2 concentration in the flue gas at the entry. The most commercially available SO_2 scrubbing systems, generally known as the Flue Gas Desulphurization (FGD) systems are not efficient enough to meet this stringent SO_2 concentration before the flue gas is being introduced into to the CO_2 capture system. The situation is further complicated for the system that has installed FGD already since it would require an auxiliary FGD system for qualifying the flue gas stream in respect of SO_2 to be ready for the CO_2 capture system and in turn increase the capital cost of the overall CO_2 capture system (McLarnon and Duncan 2009).

Oxygen present in the flue gas would pose another problem of rapid degradation of some of the alkanolamines used for amine absorption. This is commonly called as the oxidative degradation. The byproducts produced from the degradation lead to corrosion problems that cause significant deterioration in the overall separation performance. The details of this aspect are described elsewhere in the literature (Bandyopadhyay 2011).

An important feature of the post-combustion CO_2 absorption process is the high-energy requirement that results in penalty on power cycle efficiency. For instance, a power plant of 1000 MW capacity would yield net 700 MW power with 30% energy penalty. This is primarily owing to the heat necessary to regenerate the solvent in steam stripping and to some extent the electricity required for (i) liquid pumping, (ii) the flue gas fan, and finally (iii) the compression of the CO_2 produced. The performance of coal-fired TPP with various options of CO_2 capture is presented in Table 2 (Ciferno et al. 2005). In essence, the CO_2 capture plant designed for deployment should be able to generate lower CO_2 emission than the CO_2 is being captured by it for satisfying the GHG emission mitigation potential.

Table 2 Performance of coal-fired thermal power plant (TPP) with various options (adapted from Ciferno et al. 2005)

Solvent	None	MEA	Aq. NH_3	Aq. NH_3
Component(s) removed	None	CO_2	CO_2	CO_2, SO_2, NO_x, Hg
Total gross power (MW)	425	492	478	482
Auxiliary load (MW)	25	92	78	82
Net power (MW)	400	400	400	400
Coal flow rate (TPD)	3480	4895	4172	4200
CO_2 captured (TPD)	–	10,240	8727	8789
Fertilizer production (TPD)	–	–	–	443
CO_2 capture efficiency (%)	–	94	99	99
Energy penalty (%)	–	29	17	17

Energy penalty: percent decrease in power plant efficiency due to CO_2 capture

5 Cansolv Scrubbing Systems for CO_2 Capture and Sequestration Projects

Cansolv Technologies Inc. of Montreal, Canada is a global leader in amine-based post-combustion CO_2 capture and/or SO_2 scrubbing. Cansolv absorbents for CO_2 capture are designed to exhibit (i) fast kinetics—similar to primary amines, (ii) very low degradation—similar to tertiary amines, (iii) high resistance against oxidation and free radical attack, and (iv) lowest possible regeneration energy—similar to formulated amines (Birnbaum 2007). The CO_2 capture technology has been designed and developed for cryogenic storage followed by transportation for EOR and geologic storage. Figure 1 (Birnbaum 2007) shows the schematic of Cansolv CO_2 capture flow sheet. The estimated utility costs for steam (3.5 barg), electricity, and cooling water are \$5.56/t, \$0.06/t, and \$0.04/t, respectively, with 12% Cost of Capital for 25 years for a typical CO_2 capture plant. With the utility cost for a 300 MW power plant having 11% CO_2 at the inlet and flow rate of flue gas of 1.2 MMNm^3/h, the CO_2 removal is reported to be 90% with 5600 TPD of CO_2

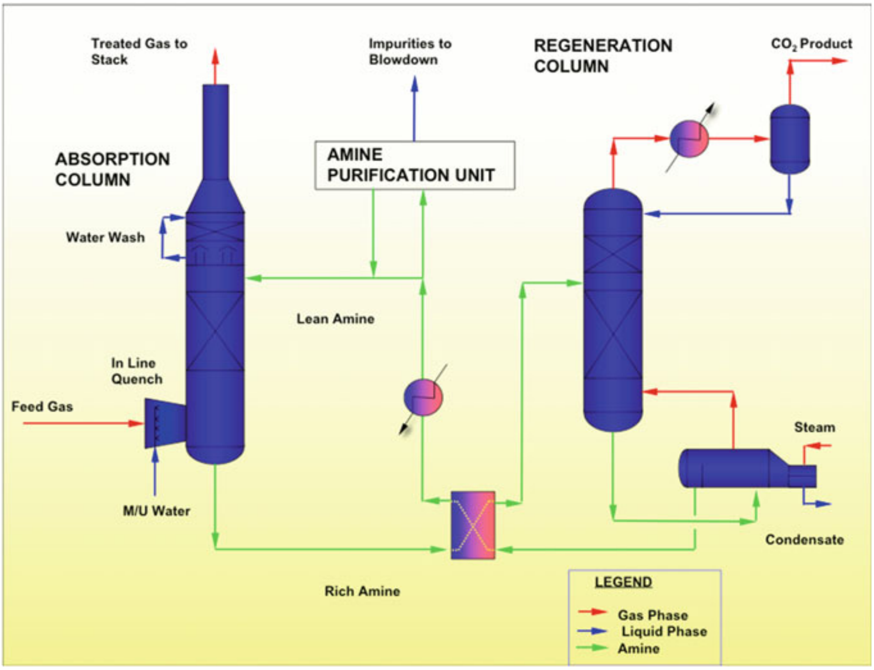

Fig. 1 Schematic of Cansolv CO_2 capture flow sheet (adapted from Birnbaum 2007)

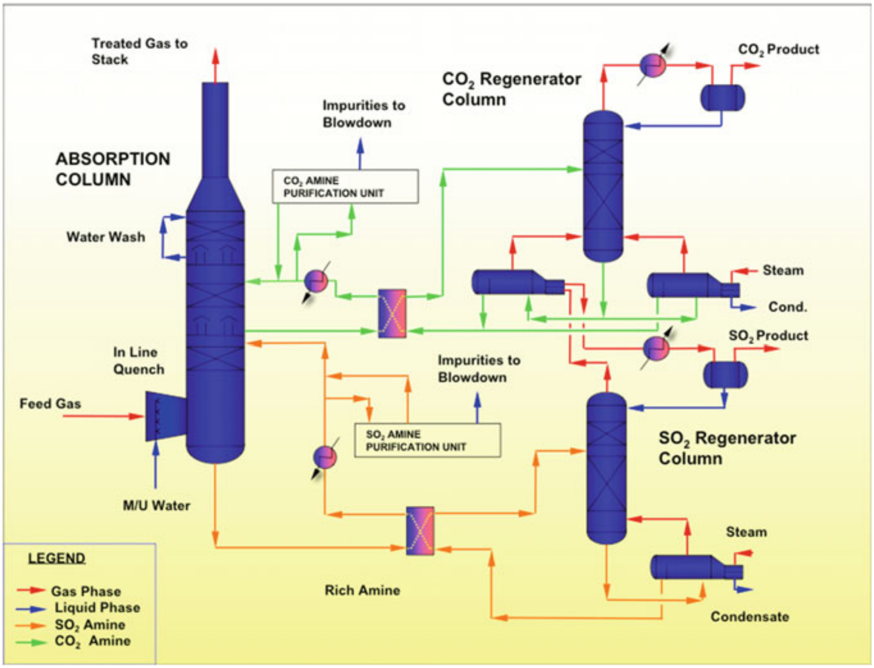

Fig. 2 Schematic of technology for simultaneous capture of SO_2 and CO_2 (adapted from Birnbaum 2007)

captured. The integrated SO_2 and CO_2 capture technology of Cansolv has been developed for fuel value-based projects that take the advantage of cost differential between premium fuels and low-value high sulfur fuels. It integrates absorbers into one vessel regenerating SO_2 and CO_2 simultaneously. The schematic of the capture technology for simultaneous scrubbing of SO_2 and CO_2 is shown in Fig. 2 (Birnbaum 2007). The absorbent used in each of the scrubbing loops comprises at least one tertiary amine and at least one secondary amine as an activator. In fact, the process developed by Hakka and Ouimet (2006), was patented for Cansolv Technologies Inc. This method recycles about 80% of heat used for SO_2 stripping into CO_2 stripping whereby a unit CO_2 capture cost reduces. Furthermore, the SO_2 concentration is reduced to a lower level however, the method is more complicated and cost intensive than simple amine (such as MEA) based capture processes.

6 Ecotoxicity Criteria of Absorbents

The ecotoxicity of the absorbents has so far been reported by Svendsena et al. (2011). In this chapter major issues reported therein are being briefly described. Amine absorption plants for CO_2 capture inherently generate degradation products of absorbents. The degradation products need reclamation or treatment (US EPA 2009). This capture plant also emits some amount of amines into the surrounding environment. Emission of amines would be allowed such that it does not have any deleterious effects on the environment. The uses of chemicals are generally covered under the provisions of the OSPAR (Oslo and Paris) Convention for the Protection of the Marine Environment of the Northeast Atlantic which is summarized in Table 3 (Svendsena et al. 2011). It is further reported that researches were carried out to study the effects of the most used, and the more exotic, absorbents (Choi et al. 2010). In that study, a marine biodegradation test following the OECD guidelines for the testing of chemicals (Test No. 306: Biodegradability in Seawater) (OECD Guidelines 1992), as well as a marine phytoplankton test with *Skeletonema Costatum* following the guidelines of ISO entitled "Water quality—Marine algal growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornutum*" (ISO/DIS-10253 2006) was considered. Many absorbents were shown to offer too low biodegradability, while others were negative to the ecotoxicity test. In the light of these observations, the absorbent structures are being pursued for finding relationship with the ecological parameters with QSAR studies (Patent CN 2011) in addition to performing bioaccumulation studies.

Table 3 Ecotoxicity criteria as per OSPAR convention for solvent selection (adapted from Svendsena et al. 2011)

Category	Criteria—ecotoxicity tests	Actions
BLACK	List of chemicals for priority action	Not discharged
	Both low biodegradability and high bioaccumulation	
	Compounds expected to be carcinogenic/mutagenic	
RED	Inorganic chemicals with high toxicity	Phased out or replaced
	Organic chemicals with low biodegradability	
	Organic chemicals/mixtures meeting two of the three criteria: Biodegradability <60%, Bioaccumulation potential (Log $K_{OW} \geq 5$), or toxicity of EC50 or LC50 $\leq$ 10 mg/L	
YELLOW	Include compounds which based on their characteristics are not defined as RED or BLACK	Accepted
GREEN	Chemicals expected to have no environmental effects	No testing

7 Chemistry of CO_2 Absorption in Aqueous NH_3

The chemistry of CO_2 absorption in aqueous NH_3 has been described in detail in the literature (Bandyoapdhyay 2011). Briefly, the main aspects are described here. The CO_2 can be removed by NH_3 scrubbing through chemical reactions at various temperatures and operating conditions (Brooks and Audrieth 1946; Brooks 1953; Hatch and Pigford 1962; Shale et al. 1971; Koutinas et al. 1983; Valenti et al. 2009; He et al. 2010) that are summarized as follows:

$$\begin{aligned}2NH_{3(g/aq)} + CO_{2(g)} + H_2O_{(1)} &\leftrightarrow CO_3{}^{2-}{}_{(aq)} + 2NH_4{}^{+}{}_{(aq)}\\ &\leftrightarrow (NH_4)_2CO_{3(aq)}[NH_3/CO_2 \text{ molar ratio} = 0.5]\end{aligned} \tag{5}$$

$$(NH_4)_2CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \leftrightarrow 2NH_4{}^{+}{}_{(aq)} + 2HCO_3{}^{1-}{}_{(aq)} \tag{6}$$

$$NH^{+}_{4(aq)} + HCO_3{}^{1-}{}_{(aq)} \leftrightarrow NH_4HCO_{3(aq)} \leftrightarrow NH_4HCO_{3(s)} \tag{7}$$

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow HCO_3{}^{1-}{}_{(aq)} + H^{+}_{(aq)} \tag{8}$$

$$HCO_3{}^{1-}{}_{(aq)} + NH_{3(aq)} \leftrightarrow NH_2COO^{-}_{(aq)} + H_2O_{(l)}[NH_3/CO_2 \text{ molar ratio} = 1.0] \tag{9}$$

$$NH_2COO^{-}_{(aq)} + CO_{2(g)} + 2H_2O_{(l)} \leftrightarrow 2HCO_3{}^{1-}{}_{(aq)} + NH_4{}^{+}{}_{(aq)} \tag{10}$$

$$NH_2COO^{-}{}_{(aq)} + NH_4{}^{+}{}_{(aq)} \leftrightarrow NH_2COONH_{4(aq)} \tag{11}$$

All the above reactions occur at atmospheric pressure however, these are very temperature sensitive. Equations (5) and (6) describe the absorption or capture of CO_2 occurring inside the absorber, while Eq. (7) represents the precipitation of the NH_4HCO_3 salt that occurs at low temperature. In contrast, Eqs. (8) and (9) representing the formation of NH_2COO^- ion may lead to an undesirable CO_2 capture and in that Eq. (10) describing the regeneration necessitates a greater enthalpy of reaction. Alternatively, NH_2COO^- ion may combine with NH_4^+ ion as per Eq. (11).

Clearly, it can be seen from these reactions that different ammonium salts can be obtained followed from the different reaction conditions (such as temperature, pressure, and concentration of reactants). These different salts can be illustrated comprehensively by the following equation (He et al. 2010):

$$\begin{aligned}aNH_3 + bCO_2 + cH_2O \rightarrow NH_4HCO_3; (NH_4)_2CO_3.H_2O; 2NH_4HCO_3(NH_4)_2CO_3;\\ NH_4COONH_2\end{aligned} \tag{12}$$

All these products are white solids and may be a single salt or mixed salts.

8 NH_3 Based Versus Amine (MEA) Based CO_2 Capture Systems

The NH_3 based and amine (MEA) based CO_2 capture systems are compared elaborately by Bandyopadhyay (2011), the major issues are summarized here. The chief disadvantages of the conventional amine (MEA) based CO_2 capture process are (a) lower CO_2 loading capacity (mol CO_2 absorbed/mol absorbent), (b) oxidative degradation of MEA by SO_2, NO_x, and O_2 in the flue gas necessitating higher liquid flow rate; (c) higher rate of corrosion; and (d) higher heat duty required for the stripper column for regenerating the absorbent. On the other hand, the major advantages of the aqueous NH_3 based CO_2 capture process are (a) higher CO_2 loading capacity; (b) devoid of corrosion problem; (c) no oxidative degradation of aqueous NH_3 by other gases present in the flue gas; (d) requiring lower liquid flow rate; (e) multipollutant capture capability, especially SO_2 and NO_x removal could be integrated with the process of CO_2 removal to yield valuable products like NH_4HCO_3, $(NH_4)_2SO_4$, NH_4NO_3 that can be put into soil as fertilizer, thus eliminating the pretreatment necessary as in amine-based processes; NH_3 based multipollutant capture system for a TPP is schematically shown in Fig. 3 (Ciferno et al. 2005) that demonstrates the capability of the multipollutant capture; (f) less energy consumption for solvent regeneration; (g) relatively more economic than MEA and other amines; and (h) major product (NH_4HCO_3) produced can be easily transported similar to other solid products without any extra investment as is often required for "pipeline transportation of compressed CO_2". Thus the solid reaction product produced in the NH_3 scrubbing of CO_2 can be (a) easily shipped to the site for Deep Ocean or geologic storage, (b) sold for EOR and Enhanced Coal Bed

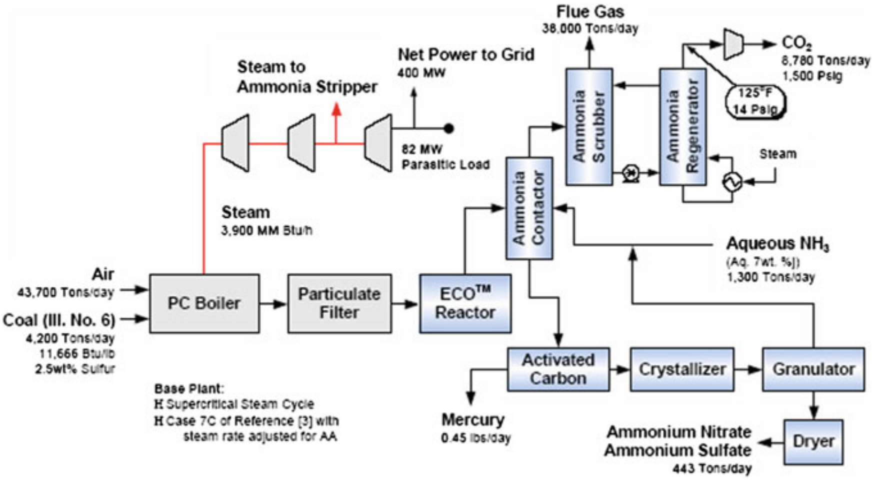

Fig. 3 Schematic showing the multipollutant control system using NH_3 for coal-fired TPP (adapted from Ciferno et al. 2005)

Table 4 CO_2 capture operating features: NH_3 versus MEA

Parameters	NH3 absorption	MEA absorption
Absorber conditions	−25 °C; 1 atm	MO °C; 1 atm
Thermal degradation	Negligible	Vulnerable
Oxidative degradation	Negligible	Vulnerable
Chemical stability	Stable	Form heat stable salts
Corrosion	Low	Significant
Volatility	High	Low
Energy input	Low	High
Cost of absorbent	Cheap	Expensive
Absorption capacity	High	Low
Multipollutant capture	No Pretreatment	Pretreatment must

Methane (ECBM) recovery applications, and (c) sold for agricultural use as conventional fertilizer (Zhou et al. 2009). The operating features of the CO_2 capture of NH_3 versus MEA processes are summarized in Table 4 (Resnik et al. 2004) for ease of understanding.

9 Major Issues for Commercialization of Aqueous NH_3 Based CO_2 Capture

9.1 Chilled Ammonia Process

Ammonia slip is the main problem in its use for CO_2 capture processes. In order to reduce such loss owing to slip NH_3 is attempted to be used under chilled condition commonly called as chilled ammonia process (CAP). This process is elaborately reviewed elsewhere in the literature (Bandyopadhyay 2011) some of which are briefly discussed here.

The use of CAP for the capture CO_2 was patented in 2006 (Gal 2006). In this process, the operating temperature was preferably specified in the range of 0–10 °C, while the pressure was close to atmospheric. The main objective in operating the process at this low temperature is to prevent the slip of NH_3 due to evaporation. The flue gas containing CO_2 is therefore, needed to be cooled at first. This is achieved in direct contact coolers at the entry to the capture plant. The capture plant comprises CO_2 capture and regeneration systems containing absorption and desorption columns in tandem. The CO_2-rich cold flue gas enters at the bottom of the absorber, while at the top countercurrently CO_2-lean solvent stream enters. The typical NH_3 concentration in the solvent was fixed to 28% (w/w). It was further specified in the patent that the CO_2 loading capacity of the CO_2-lean stream would preferably be ranging between 0.33 and 0.67.

It was claimed therein that the maximum CO_2 removal would be >90%. The exit gas, after washing with the cold water followed by acidic solution for eliminating the residual NH_3 mainly comprises nitrogen (N_2), oxygen (O_2), and fairly low concentration of CO_2. The CO_2-rich stream is finally pressurized and pumped to a desorber, preferably at temperature in the range of 100–150 °C, and at pressure in the range of 2–136 atm. In 2006, Alstom initiated a 5-year developmental program of CAP for its commercialization (Valenti et al. 2009).

9.2 Amines as Additives in NH_3 Scrubbing of CO_2

Ammonia as a solvent with functional additives, such as alkanolamines (like primary, secondary, tertiary, and sterically hindered amines) were extensively investigated for CO_2 capture as an alternative to the CAP to reduce the loss of NH_3 owing to evaporation (Seo and Hong 2000; Ali et al. 2002; Ali 2005; Paul et al. 2007). An example is cited here for the broad perspective of the readers. You et al. (2008) selected the sterically hindered amines like AMP, 2-amino-2-methyl-1,3-propandiol (AMPD), 2-amino-2-ethyl-1,3-propandiol (AEPD), and tri (hydroxymethyl) amino methane (THAM) due to the lower heat duty required for regenerating the modified solvents. Batch experiments were performed in a batch bubbling reactor using 15% CO_2 with the NH_3 concentration of 10% for NH_3 as absorbent. On the other hand, the blended absorbents were all composed of 10% NH_3 + 1% respective amine. It was reported that NH_3 loss due to vaporization was decreased in the order as: NH_3 > (NH_3 + AMPD) >(NH_3 + AEPD) > (NH_3 + AMP) > (NH_3 + THAM). It was further showed from the batch experimental results that the CO_2 removal efficiencies were slightly increased in using aqueous blended NH_3 in the order as: NH_3 < (NH_3 + THAM) < (NH_3 + AEPD) < (NH_3 + AMP) < (NH_3 + AMPD). The enhancement of CO_2 removal efficiencies reported were attributed due to the intermolecular interactions between the additives and CO_2. Clearly, amines as additives to aqueous NH_3 could be beneficial for CO_2 capture toward reduced slippage of NH_3 and enhanced CO_2 removal efficiency.

9.3 Current Status of Researches on Different Gas–Liquid Reactors Used in the CO_2–NH_3 Absorption Experiments

The different gas–liquid absorbers studied for CO_2–NH_3 system by legion of researchers are schematically shown in Fig. 4 (Zhao et al. 2012). The overall ranges of parameters included were NH_3 concentration: 0.02–35%; NH_3 volume: 125–1500 mL; NH_3 flow rate: 0.12–5 L/min; CO_2 concentration: 7–16%; CO_2 flow rate: 0.5–13 L/min; temperature: 25–35 °C; performance: 0.039–1.86 gCO_2/gNH_3; CO_2 removal efficiency: 44–99%. However, CO_2 capture could well be investigated in a

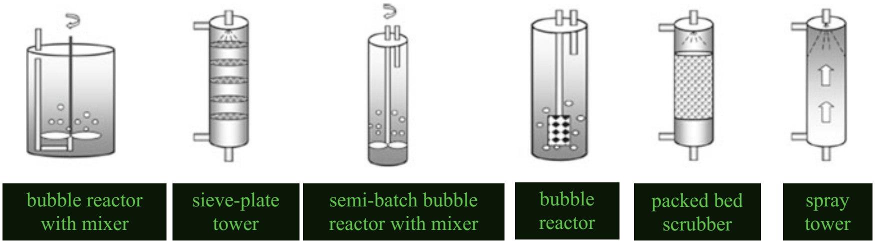

Fig. 4 Schematic showing the different CO_2–NH_3 absorption devices (adapted from Zhao et al. 2012)

low energy tapered bubble column reactor that can be operated either under batch or under continuous modes of operation. In the batch operation, gas containing CO_2 could be bubbled through a batch of quiescent liquid containing aqueous NH_3, while in a continuous operation both the CO_2 as well as the aqueous NH_3 could be flowing through the system. Such a tapered bubble column has been investigated in the recent years for studying the (i) hydrodynamics, (ii) interfacial area of contact (using CO_2–NaOH system), and (iii) removal efficiencies of fly ash and/or SO_2 (Bandyopadhyay and Biswas 2011a, b). The same system is proposed to be an interesting option for investigating CO_2 capture using promising solvents. The system developed is energetically highly favorable than other bubble column reactors. The schematics showing the continuous as well as batch modes of operation of tapered bubble column are presented in Fig. 5 (Bandyopadhyay and

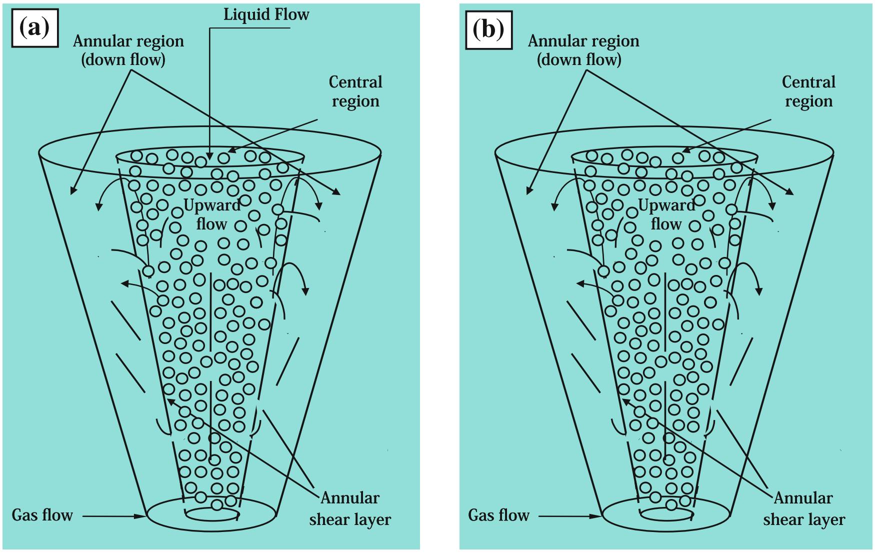

Fig. 5 Schematic of the tapered bubble column **a** continuous operation, **b** batch operation

Table 5 Advantages and disadvantages of different alkaline approaches for post-combustion CO_2 capture (adapted form Zhao et al. 2012)

Approach	Advantages	Barriers to application
Strong alkaline Alkaline metal solution (KOH, NaOH solution)	• Fast reaction rate	• Cost of absorbent
	• Large absorption capability	• Strong corrosion to equipment
	• High absorption efficiency	• Product treatment and disposal
Weak alkaline Aqueous ammonia, $NH_3{\cdot}H_2O$	• Large absorption capability and high loading capacity	• Easy to volatilize and leak
	• Low energy requirement for absorbent regeneration	• Thermal instability of products
	• Utilization of products as fertilizer • Wide distribution of absorbent	• Corrosion to equipment
Aqueous ammines (MEA, DEA, TEA, MDEA and PZ)	• Less volatile	• Absorption efficiency
	• Good stability of absorbent	• High energy consumption for regeneration
	• Enhancement role used as additive	• Easy degradation by SO_2 and O_2 in flue gas
		• Resulting in system corrosion

Biswas 2011a, b). The various advantages and disadvantages of different alkaline solutions used for post-combustion CO_2 capture are presented in Table 5 (Zhao et al. 2012).

9.4 Characterization of ABC Obtained from NH_3 Capture of CO_2 and Other Environmental Considerations

Meng et al. (2005) reported that the ABC produced using aqueous NH_3 to capture CO_2 would be an inexpensive nitrogen fertilizer. In the NH_3–CO_2 reaction, different ammonia–carbon compounds might be produced as mentioned earlier due to varied reactant concentrations reaction conditions. It is imperative to characterize the ABC thus produced by various analytical methods. It was reported that the Fourier Transform Infrared Spectroscopy (FTIR) could be used to identify the ammonium carbamate, while the X-ray diffraction could be used to distinguish ABC qualitatively from other possible products. Different samples of ABC obtainable from a bench-scale scrubber were identified by them using the carbon-hydrogen-nitrogen elemental analysis and near-infrared (NIR) spectroscopy. Finally, the quality of the

ABC obtained complied as a fertilizer under the provisions of the Agricultural Ammonium Bicarbonate National Standard of China (GB-3559-92).

Cheng et al. (2007) performed experiments for investigating the fate of carbon using the ^{14}C tracer technique upon wheat as the study plant grown on an indoor green house. The ABC synthesized from the NH_3 based CO_2 capture was applied as a potential fertilizer that was used as a crop in China for the last 30 years, while the carbon distribution was studied using the laboratory synthesized $NH_4H^{14}CO_3$ as N-fertilizer. It was reported that 76% of the unused carbon of $NH_4H^{14}CO_3$ was percolated into the soil as environmentally benign calcium carbonate ($CaCO_3$), while 88% of the carbon from NH_4HCO_3 existed in insoluble $CaCO_3$ in the alkaline soil. The carbon being trapped into the soil was increased with the soil alkalinity resulting into higher capacity to store carbon in alkaline soil. In contrast, the percentage of $CaCO_3$ in the soil was reported to be low in acidic soil to a level of 10–25%. The release of carbon to air or loss was about 20–50% and was worst in acidic soil. It was further reported that up to 10% of the carbon source was absorbed by the wheat with increased biomass production stemming from the biological assimilation and metabolism in wheat.

Lee and Li (2003) reported that the result of using NH_4HCO_3 and $(NH_2)_2CO$ as fertilizers could be different as well as beneficial. Carbonated groundwater generally would not cause any health hazards, and hence carbonates (e.g., $CO_3{}^{2-}$ and $HCO_3{}^{-}$) are harmless species unlike $NO_3{}^{-}$. Moreover, the groundwater movement could carry away carbonates further down below the earth subsurface about 500–1000 m, where they could get deposited stemming from mineral carbonation. Additionally, the groundwater residence time could be on the order of about hundred to thousands of years in many geological areas (Plummer et al. 1983). Thus the carbonates generated from the fertilizers once enter into this groundwater, they most unlikely would return back to the atmosphere within hundreds of years, even in the event of their deposition after mineralization as carbonates. The carbonates under this condition would remain in the groundwater as free carbonates. Therefore, the sequestration of CO_2 routed through this groundwater could take place significantly in many land areas, so long as the carbonates could percolate efficiently from soil into groundwater (Fig. 6; Lee and Li 2003).

It was further demonstrated by Lee and Li (2003) that the solidification of CO_2 could be achieved by acid ($HCO_3{}^{-}$) and base ($NH_4{}^{+}$) reaction utilizing insignificant amount of energy. The products obtainable from this process such as NH_4HCO_3 and $(NH_2)_2CO$ have proven market values as fertilizer. In this light, the cost of this CO_2 capture has shown to be much lower than others. The TPPs can earn profit with this technology. Furthermore, the transformation of the two industrial GHG emitters (the fossil fuel fired TPP and the fertilizer industry) into a techno-enviro-economically feasible system could be potentially achievable with the proposed technology (Fig. 7; Lee and Li 2003).

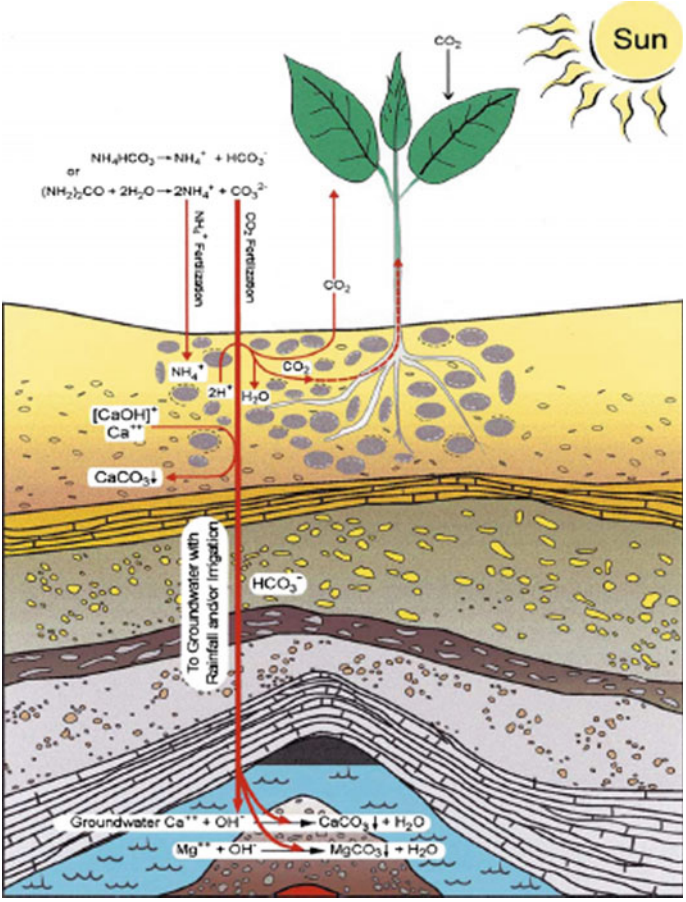

Fig. 6 Soil and subsurface CO_2 sequestration by enhanced carbonation of minerals and groundwater while using fertilizers containing carbonates (adapted from Lee and Li 2003)

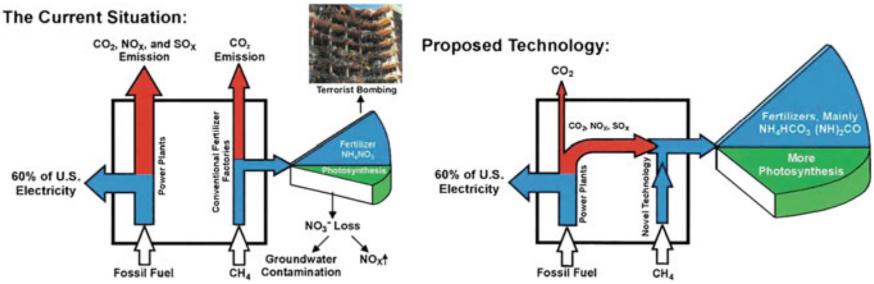

Fig. 7 The present situation is compared with the NH_3–CO_2 (flue gas) process developed showing that the technology could transform the two industrial greenhouse gases into environmentally benign systems (adapted from Lee and Li 2003)

10 Life Cycle CO_2 Emission Analyses

In this section, life cycle CO_2 emission analyses carried out between a coal-fired TPP plus NH_3 based CO_2 capture system and an equivalent ABC Plant plus an equal capacity coal-fired TPP is being discussed. The basis of the life cycle analysis is gathered from the well-known literatures (Ciferno et al. 2005; Cheng et al. 2007; Lu et al. 2007; Wang et al. 2007). Briefly, these are (i) CO_2 captured from a coal-fired TPP = 90% of 8780 t; (ii) ABC produced from captured CO_2 = 15,780.25 t; (iii) CO_2 emission from ABC after put into soil = 20% CO_2 in ABC; (iv) CO_2 emission factor of NH_3 plant = 1.22 t CO_2/t NH_3; (v) excess CO_2 emission factor from ABC plant = 0.248 t/t ABC; and (vi) electricity of ABC plant = 130 kwh/t ABC. The analysis is detailed in Table 6. The estimated CO_2 emission for a 400 MW TPP with CO_2 capture by NH_3 would be 6877.77 t, while the estimated CO_2 emission for a 400 MW TPP plus an ABC plant of equivalent capacity would be 15,416.45 t wherein the unaccounted factors could be covered by further adding 5% of the total CO_2 emission. It transpires that CO_2 capture by aqueous NH_3 from TPP has shown to reduce GHG emission considerably compared to an equivalent plant of ABC and equal capacity TPP. Thus NH_3 scrubbing of CO_2 could be beneficial so far as GHG emission is concerned and a plausible option for CO_2 capture from flue gas of TPPs. Such option may be suitable, especially in weaker economies considering its simple operation with multiple benefits. The GHG emission in t CO_2eq could be further reduced in the event of carbon management integrating NH_3 carbonation and biomass pyrolysis for producing ABC. Such an option was developed by Oak Research Laboratory (Fig. 8: Lee et al. 2001). Therefore, NH_3 based CO_2 capture system could be beneficial.

Table 6 Life cycle analysis of CO_2–NH_3 process for a coal-fired TPP

Items	CO_2 emission, *t*	
	400 MW TPP with CO_2 capture by NH_3	400 MW TPP + ABC plant of equivalent capacity
Product = ABC	15,780.25	15,780.25
TPP CO_2 emission	976.60 [10% of Total]	8104
CO_2 emission from ABC	1757.80	1757.80
CO_2 from NH_3 Plant	4142.82	3913.50
CO_2 from electricity for ABC Plant	Covered under CO_2 capture plant	1641.15
Grand total	6877.77	15,416.45
Unaccounted factors could be covered by further adding 5% of the total CO_2 emission		

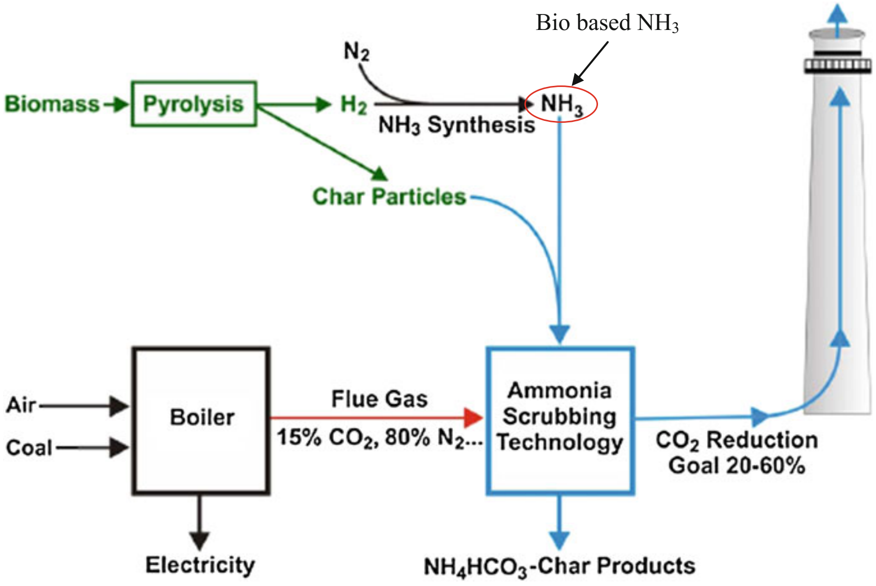

Fig. 8 Effective carbon management integrating carbonation of NH_3 and biomass pyrolysis (adapted from Lee et al. 2001)

11 Barriers in Operating Traditional Amine-Based CO_2 Capture Technology

Legion of researches have so far been carried out nationally and internationally since long back on amine-based CO_2 absorption processes. But the information on the effects of relevant amines on fauna is scanty. However, laboratory experiments on animals revealed that amines were irritating to skin and toxic at high concentrations. Further, amines might produce eutrophication on vegetation as well (Aarrestad and Gjershaug 2009).

Knudsen et al. (2009) reported that the amine-based CO_2 capture plant would emit amines into the ambient air, and could possibly also form other compounds after emission in the atmosphere. The widely studied amines were MEA (monoethanolamine or 2-amino ethanol), AMP (2-amino-2-methyl-1-Propanol), MDEA (methyl diethanolamine or 2,2′-(methylimino) bis-ethanol), and Piperazine. The major concerns are the formation of toxic compounds such as nitrosamines, nitramines, and amides by the reaction of amines with oxidized nitrogen compounds such as NO_x present in the ambient air. Investigation was conducted to develop the understanding of the atmospheric amine chemistry for assessing the impacts of the amine emissions, stemming from the CO_2 capture plant that uses amines, to human health and surrounding environment. The findings of the investigation of Knudsen et al. (2009) were as follows:

- It was reported that nitrosamines, nitramines, aldehydes, and amides were formed as the main photooxidation products of amines. These compounds might be posing a potential risk to human health and surrounding environment.
- Nitrosamines were of prime concern that could be toxic and carcinogenic too at extremely low concentrations.
- Nitramines were also of concern as these were suspected to be carcinogenic, though significantly less potent than the nitrosamines. Higher exposure levels observed might be due the longer lifetime in the atmosphere.
- Atmospheric dispersion models showed that amine emissions could have adverse impacts at both local and regional scales.
- Theoretical modeling further indicated that amines could lower the surface tension of water droplets and under certain climatic conditions it could trigger rainfall causing negative impacts to the local environment.
- Results from a worst-case scenario of emissions from a full-scale amine-based CO_2 capture plant with environmental conditions representing the West Coast of Norway, revealed that the predicted ground-level concentrations of the suggested photooxidation compounds were at the same order of magnitude as the proposed "safety limits", indicating that risks to human health and environment could not be ruled out.

In another study, the potential side effects of the amine-based CO_2 capture process stemming from a small fraction of unintentional release of amine into the atmosphere were reported (Dautzenberg and Bruhn 2013) as follows:

- The formation of the carcinogenic nitramines and nitrosamines could cause risk of exposure (direct or via soil, ground water);
- The formation of secondary aerosols might lead to the risk for human health, climate forcing potential, air pollution/visibility;
- The production of tropospheric ozone (an irritant gas) could cause plant damages and crop yield reduction, climate forcing potential; and
- The risks associated with the hazardous wastes generated from the spent amine (incineration of which would lead to emission of CO_2, H_2O, and even N_2O, while biodegradation would be costly—these demand further experimental investigations).

The possible impacts are, however, strongly dependent on the types of amines used in the CO_2 capture process and the quantum of emissions of amine into the air. Therefore, operating an amine-based CO_2 capture plant either with known solvents or with solvents (like blended hindered amines) covered under patented rights could have serious health damages that are prohibitively costly. Additionally, management of the spent solvent as hazardous waste complicates the overall carbon footprint.

12 Recommendations Put Forward for Consideration by the Government of India on Suitable CO_2 Capture Technology in Indian Coal-Fired TPPs and Other Industries (Fertilizer Plants, Integrated Iron and Steel Industries, Petroleum Oil Refineries, and Cement Industries) Having Potential CO_2 Emissions from Point Stationary Sources

After careful consideration of the foregoing short critical analysis, it is suggested to avoid deployment of amine-based CO_2 capture technology to coal-fired TPPs as well as to other industrial facilities such as fertilizer plants, integrated iron and steel industry, petroleum oil refineries, cement industries, and similar other CO_2 emitting industrial sources in India. In this light, following recommendations are being put forward as better alternatives to the traditional amine-based CO_2 capture technology for capturing CO_2 from the exhaust flue gas of Indian TPPs as well as other Indian industrial sources mentioned earlier.

12.1 Technology Development

12.1.1 Use of Aqueous NH_3 (Either at Chilled Condition in CAP or at Room Temperature with Low Concentration)

It is reported that the maximum hourly concentration of NH_3 emission in the CAP was 55 $\mu g/m^3$ under worst-case scenario (Dautzenberg and Bruhn 2013). The emission of NH_3 from an aqueous solution of NH_3 at room temperature would be slightly higher than the estimated emission for CAP. It could however, be reduced by acid wash, if needed. Presumably, the 24 hourly concentrations would be less than the maximum (worst) value reported. The concentration of NH_3 however, could be further reduced at the ground level owing to dispersion. Therefore, it can be qualitatively predicted that the maximum ground-level concentration of NH_3 in and around NH_3 based CO_2 capture plant would be well within the 24 hourly value of 400 $\mu g/m^3$ stipulated under the National Ambient Air Quality Standards (NAAQS) of India. This aspect could however, be examined from an operating CO_2 capture plant at pilot scale using aqueous NH_3 developed indigenously to ascertain the magnitude of source emission followed by quantification of NH_3 concentration at the ground level.

Application to Coal-Fired Thermal Power Plant

The end products of scrubbing of flue gas (containing CO_2, SO_2, NO_x and uncollected fly ash) using aqueous NH_3 from the coal-fired TPP would be ammonium bicarbonate [NH_4HCO_3] (ABC), ammonium sulfate [$(NH_4)_2SO_4$], and ammonium nitrate [NH_4NO_3]. These products have the potential to serve as N-fertilizer. In addition to the solid reaction products, the uncollected fly ash from the highly efficient electrostatic precipitator could serve as micronutrients as detailed earlier.

Under the above circumstances, multisectoral research programs are proposed here in a planned manner for making the use of the available resources in the country with the coordinated approach of few important streams such as academia, thermal power, fertilizer, agriculture, environment, and climate change for developing indigenous NH_3 based CO_2 capture technology. The concerned Ministries of government of India are: Ministry of HRD for inducting the academic potentials, the Ministry of Power for utilizing the knowledge of the Power Plant Engineers, the Ministry of Chemicals and Fertilizers for extending the knowledge of ABC manufacturing plants and others, the Ministry of Agriculture for exploring the efficacy of land application of ABC and its concomitant products, and finally the Ministry of Environment, Forests and Climate Change to formulate the strategy for developing a technology-based regulatory standard in the form of CO_2 capture plant for the coal-fired TPPs in India. The scope of Indian Research and Development (R&D) based on NH_3 based CO_2 capture technology is shown in Fig. 9. It is highly

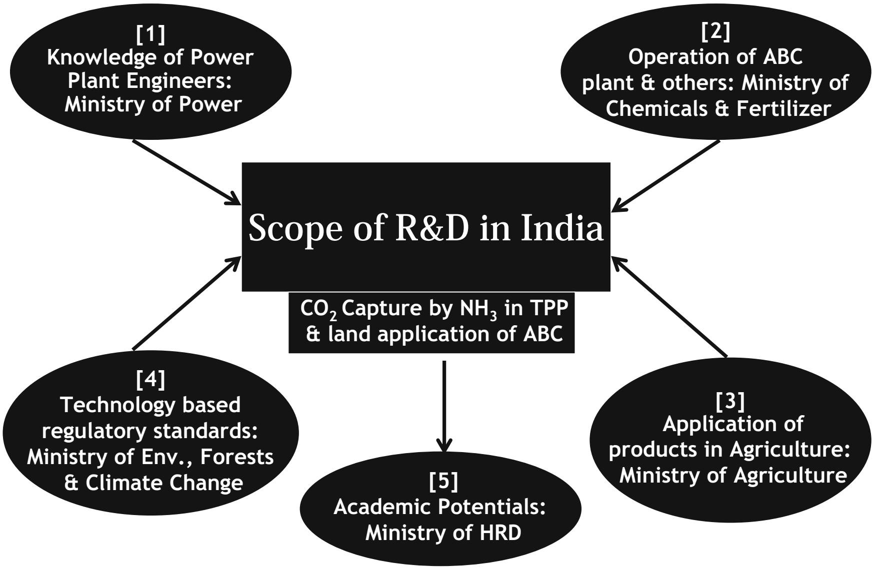

Fig. 9 Scope of multisectoral R&D in India for CO_2 capture using NH_3

recommended that the NH_3 based CO_2 capture process may further be explored through R&D in India.

Application to Fertilizer Plant

Ammonia scrubbing could be applied to fertilizer plants for capturing CO_2 replacing the current method of amine-based CO_2 capture. Ammonium bicarbonate produced could be heated to generate CO_2 with high purity for use in the manufacture of urea. Otherwise, ABC could be used for the production of N-fertilizer or for the production of sodium carbonate. Research programs are also proposed in a planned manner for making use of the available and relevant resources in the country for developing indigenous NH_3 based CO_2 capture technology similar to that described for the coal-fired TPP.

Application to Integrated Iron and Steel Industry

Ammonia scrubbing could be applied to integrated iron and steel industry for capturing CO_2 from various sources. The ammoniacal liquor generated from the coke oven byproduct plant (COBP) could be used for this purpose instead of using NH_3 from conventional route (such as steam methane reformer) to reduce the carbon footprint. Indian steel industries under the SAIL have a proven record of manufacturing $(NH_4)_2SO_4$ in the COBP. Research programs are also proposed in a planned manner for making use of the available and relevant resources in the country for developing indigenous NH_3 based CO_2 capture technology similar to that described for the coal-fired TPP.

Application to Petroleum Oil Refinery

Ammonia scrubbing could be applied to petroleum oil refineries for capturing CO_2 from various fuel burning operations. Ammonia-based CO_2 capture could be applied here as well. Research programs are also proposed in a planned manner for making use of the available and relevant resources in the country for developing indigenous NH_3 based CO_2 capture technology similar to that described for the coal-fired TPP.

Application to Cement Industry

Ammonia-based CO_2 capture could also be applied to cement industries. Research programs are also proposed in a planned manner for making use of the available and relevant resources in the country for developing indigenous NH_3 based CO_2 capture technology similar to that described for the coal-fired TPP.

12.1.2 Use of Dilute NaOH Solution for CO_2 Capture

The sequestration of CO_2 using brines has been patented by Jones (2010) assigned to Skyonic Corporation and referred to as SkyMine process. In this process, principally CO_2 was absorbed into an aqueous solution of NaOH to form sodium carbonate (Na_2CO_3) and/or sodium bicarbonate ($NaHCO_3$) according to the following reactions in the carbonation reactor or the absorption column:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

The NaOH was produced from the electrolysis of brine solution. The flue gas from the fossil fuelled TPP was first passed through series of coolers before being introduced at the bottom of an absorption column utilizing the NaOH as the absorbent. The process has the multipollutant capture capability also due to its ability to remove effectively SO_x, NO_x and mercury from the flue gas. In addition, this method offers insignificant health and safety concerns than those identified in case of amine and NH_3 based CO_2 capture processes. Application of this method to flue gas containing only CO_2 would be very much useful as in the case of CO_2 capture from the calcination of limestone for producing CaO in cement industry. The use of the end product in this situation would be easier than those obtainable in case of multipollutant capture system. For instance, the end products of NaOH scrubbing of flue gas from the coal-fired TPP would be Na_2CO_3/$NaHCO_3$, sodium bisulfite [$NaHSO_3$], and sodium nitrite [$NaNO_2$]. The use of the product mix as well as NaOH based CO_2 capture technology should be explored by undertaking specific research programs in a planned manner for making use of the available and relevant resources in the country similar to that described earlier.

12.1.3 Mineralization of CO_2 in Integrated Iron and Steel Industry

The sequestration of CO_2 can be achieved by mineralization under leakage-free condition for very long time. The various alkaline wastes rich in calcium content such as steel making slags as well as fly ash, and alkaline wastewater rich in total dissolved solids could have the potential for carbonation toward CO_2 emissions reduction option for steel plants. The calcium content in these wastes could be selectively extracted from the slags and others before carbonation followed by the production of a pure and marketable $CaCO_3$. The process is generally carried out at atmospheric pressure. Amongst the various solvents examined ammonium salt solutions (NH_4Cl, CH_3COONH_4, NH_4NO_3) as well as brine, NaOH, etc., were reported to offer promising results for carbonation of calcium of slag and others. This in turn, could reduce the consumption of the natural and synthetic $CaCO_3$ used in industry resulting into conservation of natural resources with CO_2 emissions reduction (Eloneva et al. 2009; Olajire 2013; Sanna et al. 2014; Pan et al. 2015). Various options of CO_2

mineralization could be investigated for exploring the most economic one with lowest carbon footprint. Research programs are also proposed in a planned manner for making use of the available and relevant resources in the country for developing indigenous CO_2 capture technology similar to that described earlier.

12.2 Development of Centre for CO_2 Capture and Carbon Engineering

A "Centre for CO_2 Capture and Carbon Engineering" may be established under the aegis of Climate Change Research Institute with support from the Ministry of Earth Sciences in India for developing indigenous CO_2 capture technology as proposed. The center may be located in and around the industrial region or in the urban city in the country.

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