

CO2 Mitigation

Ganesh Ugale¹, Pratik R. Borse², Sanket J. Amrutkar³, Hemant R. Sonawane⁴

^{1, 2, 3, 4}Chemical Engineer, Loni, Maharashtra, India

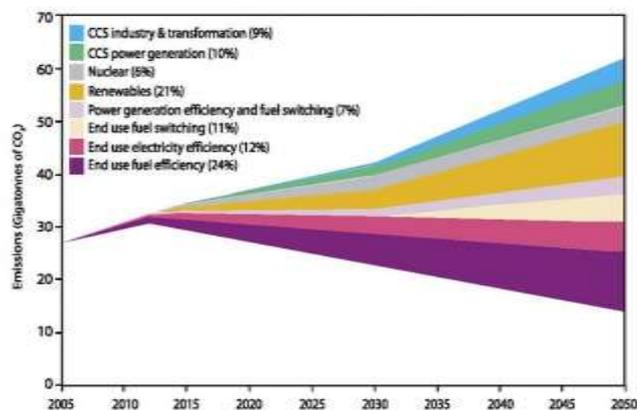
Abstract - Carbon Dioxide(CO₂) with increasing the crisis for ecology and nourishing to extinguish the planet also known as the greenhouse gas. The power plants play the major role to the emission of the flue gas containing CO₂. To evade such environmental issue with its mitigation by the methods of pre as well as post combustion in various power plants for the capture of CO₂ that uses amine as base. More the CO₂ accumulates in the atmosphere more the climate heats up, so to get rid of such crisis towards the environment, there was an increase in the chase of research to capture CO₂ from the environment. The post combustion method is the most widely used in various power plants and it's quite similar to the desulphurization. To overcome such technique towards future prospective by developing solid adsorbent with better stability and efficiency in the field of the nano technology, the DFNS-oxytrides can be used as the solid adsorbents for the CO₂ capture was playing a crucial role in the CO₂ mitigation with its satisfactory fibrous morphology and at another sight the integrated solar fuel system where sunlight is used to convert CO₂ and water vapour into the hydrocarbon by using photocatalytic conversion. Thus urge to remove CO₂ from atmosphere and having the recent technology of conversion of direct air to methanol with its highest efficiency by homogeneous catalyst system using pentaethylenhexamine (PEHA).

Key Words: carbon dioxide, greenhouse gas, amine, DFNS, photocatalytic conversion, methanol, homogeneous catalyst, PEHA.

1. INTRODUCTION

- CO₂ the main constituent which is contributing the green house effect upto 26%.
- After industrial revolution the climate change phenomenon has been accelerated with reliance in fossil fuels, coal and oil across the world.
- In carbon capture and sequestration amine plays a good role with its reversible reaction with CO₂ where pre and post combustion method belongs too.
- The transformation of technologies or process towards nano-science the DFNS was playing crucial role to capture CO₂.
- Overall this reusing and utilizing the CO₂ to form the hydrocarbon from where it originated.

As depicted in below graph CCS technology in the various industries & power plant can ultimately lower down the CO₂ concentration from atmosphere but as the CCS technology used in this sector which holds to reduce 19% which is just smaller than the use of renewable resources. So what if we combine both CCS technology with renewable to get it to its highest efficiency because as shown in graph we can't end up with the use of the fuels and electricity as the coal which has the highest energy producing fuel and also the fossil fuels on which the whole world is dependent. So just to have such reliance on fossil fuel we need to build up such technique that should be reusable, recyclable and spontaneously reducing the pollution too.



1.1 METHODOLOGY:-

There are various process, synthesis and technology to mitigate CO₂ to reuse and recycle it without harming environment. Apart from that we choose some of the techniques from various fields.

PRE-COMBUSTION:- It allows us to capture CO₂ and maximize power output an air separation unit produces a stream of almost pure oxygen which flows into the gasifier and reacts with fuel to form syngas which is a mixture of hydrogen, carbon monoxide (co) and water. Shift reactor converting the co to hydrogen and carbon dioxide. The CO₂ is captured from gas stream after dehydration and compression, then it is ready for transport and storage. Today hydrogen is used as fuel and also used to make electricity. The excess heat is used to power steam turbine optimizing energy output.

POST-COMBUSTION:- In post combustion method, capture of the flue gas from fossil fuels which are burned as normal but before the free gas travels to chimney that passes through the absorber column which is filled with liquid solvent called as amines which absorbs the CO₂ before it enters the atmosphere with superheated steam is then passed through chimney this releases CO₂ from the amines and can be stored in the storage tank by evolving the remained flue gas through the chimney.

DFNS (Dendritic Fibrous Nanosilica):-As it's an urge to evade the climate change phenomenon. Therefore, the rise in demand for CO₂ sorbents with high capture capacity and faster kinetics is continuously growing. This can be conceived by development of solid sorbents with improved efficiency. Porous silica functionalization by various amines is one of the best way for CO₂ sorbent materials. Ayan Maity and Vivek Polshettiwar envisioned that DFNS as a possible good support to design efficient CO₂ sorbents. Due to its open and fibrous structure, it could have high amine loading, with minimum reduction in surface area and improved amine sites accessibility. To study these hypotheses, functionalization of DFNS using various amines was carried out (as depicted in figure). Range of amine molecules such as propyl amine (PA), propylethylene diamine (PEDA), propyldiethylene triamine (PDETA), tetraethylene pentamine (TEPA) and polyethylenimine (PEI) with both low and high molecular weights (LMW and HMW) were loaded on DFNS by physisorption as well as by covalent attachment.

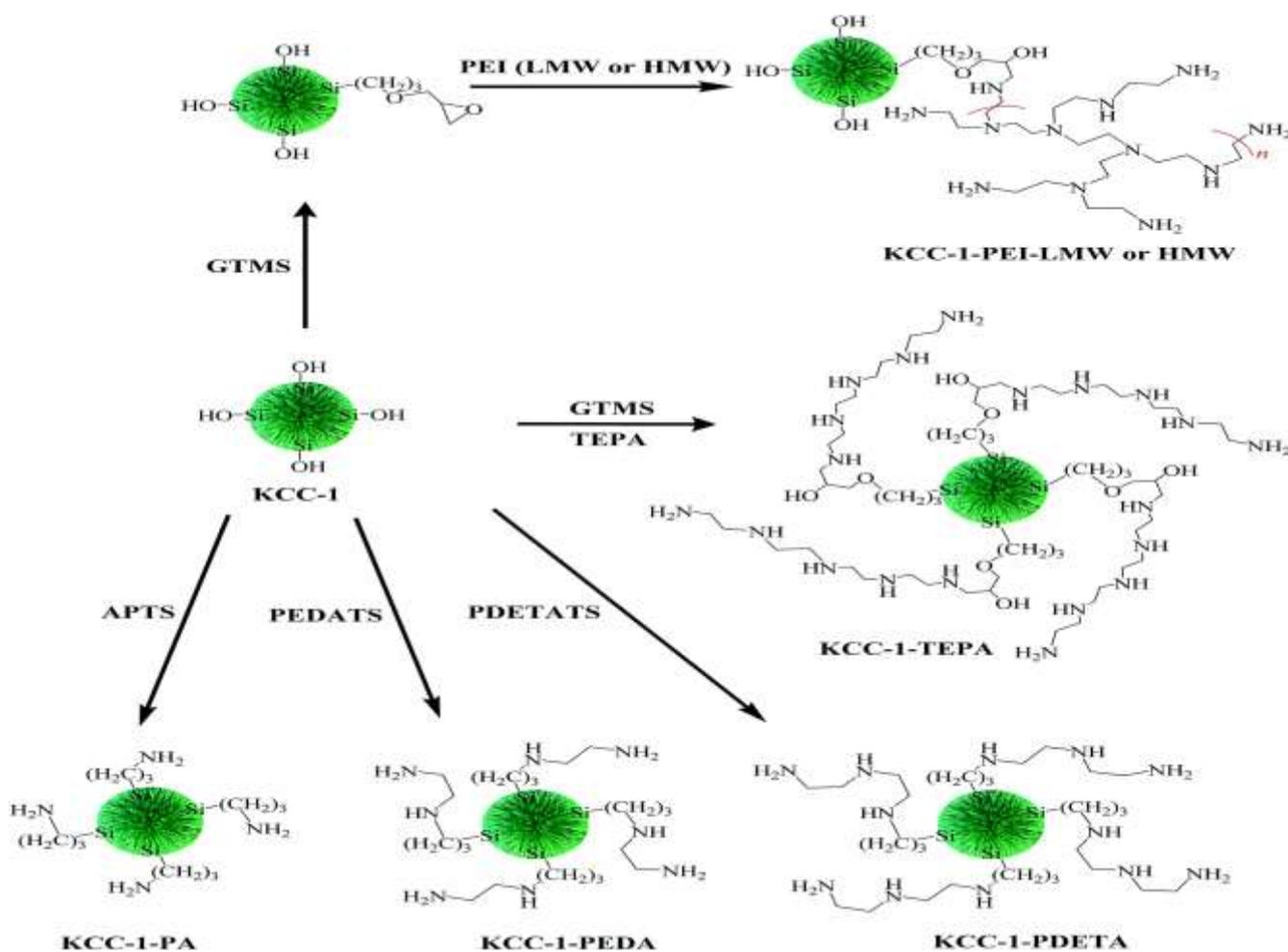


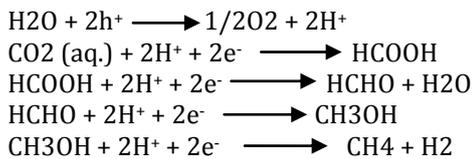
Figure 2: "Functionalization of DFNS with various amines". [4]

Photocatalytic conversion of CO₂ into Hydrocarbon.

Direct solar conversion of CO₂ and water vapor into hydrocarbon fuels using sunlight is an attractive prospect, serving to reduce atmospheric CO₂ concentrations while providing on a renewable basis an energy dense portable fuel compatible with our

current energy infrastructure. As depicted in Figure 1, we suggest a strategy of using the fuel on a closed-loop basis; fuel is burned, the CO₂ emissions are collected and passed into a photocatalytic bed where solar energy is used to convert the CO₂ back into fuel.

In 1979, Inoue and co-workers examined the use of semiconductor powders for CO₂ reduction, including TiO₂, ZnO, CdS, WO₃, etc suspended in CO₂ saturated water illuminated by a Xenon lamp. Small amounts of formic acid, formaldehyde, methanol, and methane were produced. According to Inoue suggested that CO₂ to methane conversion can be take placed in several multistep as follows-



Light Source	Catalyst	Reaction Medium	Product
UV Hg Lamp	TiO ₂ loaded zeolite	CO ₂ and H ₂ O vapor	Methanol
UV Lamp	TiO ₂ powder	CO ₂ and H ₂ O vapor	Methane, Hydrogen, CO
Natural sunlight of AM1.5 illumination	Cu, Pt co catalyzed N-doped TiO ₂ nanotube arrays	CO ₂ and H ₂ O vapor	Methane, other alkanes, olefins, Br-paraffins, H ₂ , CO.

Table -1: "Photocatalytic Reduction of CO₂". [10]

Direct Air to Methanol using polyamine and homogeneous catalyst

There is one-pot CO₂ capture and conversion to CH₃OH at relatively mild temperatures (125–165 °C) involving pentaethylenehexamine (PEHA) and a Ru-PNP complex.

It consists of directly capturing and converting a carbon dioxide from atmosphere and converting it into methanol. Thus a homogeneous catalyst is being used for hydrogenation purpose in the reaction. Several results were obtained by manipulating the data as temperature, additive and time period. Firstly CO₂ is captured from air with the help of polyamine in which the flow rate was adjusted at 200 ml/min for 64 hr. Thus the proposed reaction for this is as given-

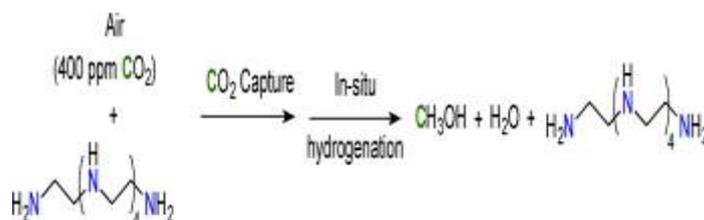


Figure 4: "CO₂ Capture from Air and Conversion to CH₃OH". [12]

Hydrogenation with the help of homogenous catalyst and carbon capture with PEHA which then further converted into methanol and the polyamine is again recovered for recycling. Following catalysts are being used for various results as shown in table no-1.

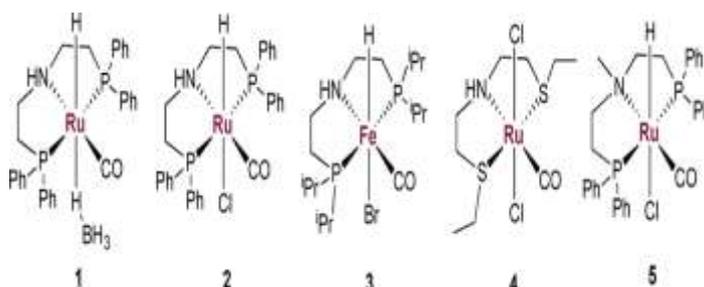


Figure 3: "Catalysts". [12]

The results depicted in below table no-1 shows the production of methanol in terms of TON (turnovernumber).

Entry	Amine	catalyst	T(°c)	Additive	CH ₃ OH (mmol)	(TON) CH ₃ OH
1	PEHA	1	95-155	K ₃ PO ₄	9	450
2	PEHA	2	95-155	K ₃ PO ₄	9.1	455
3	PEHA	3	95-155	K ₃ PO ₄	-	-
4	PEHA	4	95-155	K ₃ PO ₄	-	-
5	PEHA	5	95-155	K ₃ PO ₄	-	-
6	TMG	1	95-155	K ₃ PO ₄	-	-
7	DBU	1	95-155	K ₃ PO ₄	1.6	80
8	PEHA	1	95	K ₃ PO ₄	-	-
9	PEHA	1	95-155	-	7.6	380
10	PEHA	1	155	K ₃ PO ₄	13.8	690
11	PEHA	1	155	-	10.4	520
12	PEHA	1	155	-	21.2	1060

Table -2: "Catalyst Screening for Hydrogenation of CO₂". [14]

Reaction condition: PEHA=3.4 mmol, TMG = 8.5 mmol, DBU = 8.5 mmol, K₃PO₄ = 1 mmol, CO₂/H₂ (1:3) = 75 bar, catalyst = 20 μmol, and THF = 10 mL. Entries 1-7 and 9, 95 °C for 18 h and 155 °C for 18 h. Entry 8, 95 °C for 18 h. Entries 10-12, 155 °C for 40 h. Determined by ¹H NMR.

This shows the production of methanol were there was problem of recovering from water with the help of distillation process because of solvent being used (THF) 66°C having boiling point near to methanol(64.7°C) which having lower efficiency of separation which then being changed to triglyme, 1,4-dioxane which having boiling point 216 and 101°C respectively which changed its yield from 29 to 79% as shown in table no-3

Entry	Amine	CO ₂ captured (mmol)	Solvent	CH ₃ OH (mmol)	NMR yield(%)
1	PEHA	5.4	1,4-dioxane	2.1	39
2	PEHA	5.4	Triglyme	3.3	61
3	PEHA	5.4	Triglyme	4.3	79

Table-3: "CO₂ Capture from Air and Conversion to CH₃OH" [12]

Reaction conditions: PEHA = 3.4 mmol, catalyst 1 = 20 μmol, H₂ = 50 bar, t = 40 h, T = 155 °C, and organic solvent (10 mL)-H₂O (8 mL). bt = 55 h.

By implementing this method in a flow system, continuous production of CH₃OH can be achieved.

3. CONCLUSION

This literature includes an overall CO₂ capture methods and as the atmospheric CO₂ level is increasing. As Pre and post combustion are the traditional methods being used and are much costly and is limited up to thermal power plants. Where a new technology of reducing CO₂ with the help of renewable source and water which requires a purified carbon dioxide for synthesis thus getting inspire from these technology we are having latest CO₂ from air to methanol technique. An integration to build an environment friendly techniques for mitigation of carbon dioxide from atmosphere and converting back into useful chemicals as well as fuels from where it is being originated.

REFERENCES

- [1] Environmental Assessment of the Integration of Amine-based CO₂ Capture Unit to Coal-fired Power Plants for Greenhouse Gas Mitigation. Bhurisa Thitakamol, Amornvadee Veawab and Adisorn Aroonwilas Faculty of Engineering, University of Regina, Regina, Saskatchewan, Canada S4S 0A2 Tel: (306) 585-5665, Fax: (306) 585-4855, Email: veawab@uregina.ca
- [2] Bello, A. and R. O. Idem. Pathways for the Formation of Products of the Oxidative Degradation of CO₂-loaded Concentrated Aqueous Monoethanolamine Solutions during CO₂ Absorption from Flue Gases. Industrial & Engineering Chemistry Research 44(4): 945-969, 2005.

- [3] CO₂ Capture and for Improving Heavy Oil Recovery. Lei Tao, Zhaomin Li China University of Petroleum (East China) Dongying, China taolei2365@yahoo.com.cn Na Zhang Shengli Oilfield, Sinopec Dongying, China Henan Sun Heriot-Watt University Edinburgh, UK.
- [4] Dendritic Fibrous Nanosilica (DFNS) for Catalysis, Energy Harvesting, CO₂ Mitigation, Drug Delivery and Sensing. Ayan Maity, Vivek Polshettiwar* Nanocatalysis Laboratories (NanoCat), Department of Chemical Sciences, Tata Institute of Fundamental Research (TIFR), Mumbai, India. Email: vivekpol@tifr.res.in, ChemSusChem 10.1002/cssc.201701076.[Fig-2]
- [5] Samanta, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Post-Combustion CO₂ Capture Using Solid Sorbents: A Review. *Ind. Eng. Chem. Res.* 2011, 51, 1438-1463.
- [6] Didas, S. A.; Choi, S.; Chaikittisilp, W.; Jones, C. W. Amine- Oxide Hybrid Materials for CO₂ Capture from Ambient Air. *Acc. Chem. Res.* 2015, 48, 2680-2687.
- [7] Singh, B.; Polshettiwar, V. Design of CO₂ Sorbents using Functionalized Fibrous Nanosilica (KCC-1): Insights into the Effect of the Silica Morphology (KCC-1 vs MCM-41). *J. Mat. Chem. A.* 2016, 4, 7005-7019.
- [8] Patil, U.; Fihri, A.; Emwas, A.; Polshettiwar, V. Silicon Oxynitrides of KCC-1, SBA-15 and MCM-41: Unprecedented Materials for CO₂ Capture with Excellent Stability and Regenerability. *Chem. Sci.* 2012, 3, 2224-2229.
- [9] Radu, D. R.; Pizzi, N. A.; Lai, C. -Y. Functionalized Stellate Macroporous Silica Nanospheres for CO₂ Mitigation. *J. Mater. Sci.* 2016, 51, 10632-10640.
- [10] Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. Somnath C. Roy,† Oomman K. Varghese,† Maggie Paulose, and Craig A. Grimes*, Department of Electrical Engineering, and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802. February 8, 2010. 10.1021/nn9015423.
- [11] Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic Reduction of Carbon-Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature* 1979, 277, 637-638.
- [12] Conversion of CO₂ from Air into Methanol Using a Polyamine and a Homogeneous Ruthenium Catalyst, Jotheeswari Kothandaraman, Alain Goeppert, Miklos Czaun, George A. Olah,* and G. K. Surya Prakash*, Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661, United States. DOI: 10.1021/jacs.5b12354.[Fig-3, Fig-4]
- [13] Alberico, E.; Nielsen, M. *Chem. Commun.* 2015, 51, 6714-6725.
- [14] (a) Li, Y.-N.; He, L.-N.; Liu, A.-H.; Lang, X.-D.; Yang, Z.-Z.; Yu, B.; Luan, C.-R. *Green Chem.* 2013, 15, 2825. (b) Li, Y.-N.; He, L.-N.; Lang, X.-D.; Liu, X.-F.; Zhang, S. *RSC Adv.* 2014, 4, 49995-50002.