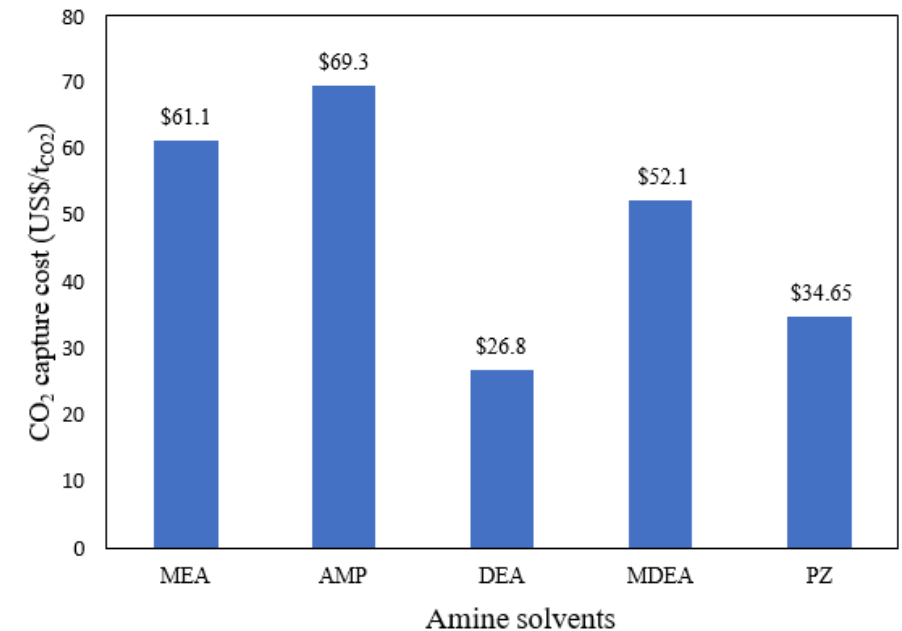


ADVANCED MATERIALS HOLD THE KEYS TO OVERCOMING BARRIERS TO VIABLE CO₂ CAPTURE

Does Your Organization Have a Pathway to Overcome the Hurdles for Developing CO₂ Capture Technologies?

TCGR's report, '*Advanced Materials for CO₂ Capture and Separation*,' is a techno-economic investigation commissioned by TCGR's **Carbon Dioxide Capture & Conversion (CO₂CC) Program** members offers guidance in the following:

- Economic analysis of CO₂ absorption, CO₂ adsorption, and membrane separation
- State-of-the-art technology development on absorption, adsorption, membrane separation and other CO₂ capture technologies
- Defining the pathways to overcome hurdles of the development of CO₂ capture technologies.



**Don't miss this opportunity to better position your organization for future decisions.
Join TCGR's CO₂CC Program today to receive this one-of-a-kind report:
One of the invaluable benefits of CO₂CC Program Membership**

ADVANCED MATERIALS FOR CO₂ CAPTURE AND SEPARATION

*A techno-economic investigation commissioned by the members of the
Carbon Dioxide Capture and Conversion (CO₂CC) Program*

Report Completed: September 2022

NEED FOR THE STUDY

- Developing new advanced materials for CO₂ capture and separation is seen as a prerequisite for improving the energy and economic viability of CCUS, reducing the cost associated with achieving net-zero targets.
- In the last half-century, the concentration of CO₂ has exhibited a dramatic growth from about 310 to over 410 ppm (parts per million) owing to the large-scale utilization of fossil fuels and various chemical refinery processes.
- Carbon capture, utilization and storage (CCUS) is currently considered a key approach to reducing the GHG emissions from the power and industrial sectors.
- The report addresses:
 - ✓ State-of-the-art technology development on absorption, adsorption, membrane separation and other CO₂ capture technologies.
 - ✓ Modification of solvents for CO₂ absorption and address the challenges of the current use of solvents.
 - ✓ Recent development in terms of the optimization of process parameters including temperature, CO₂ concentration, pressure, and flow rate.
 - ✓ Current development of reactor design and improvement for CO₂ absorption and adsorption.
 - ✓ Development of adsorbents for different temperature applications
 - ✓ New insights for CO₂ adsorption with state-of-the-art sorbents (e.g., CaO, MgO, and biochar).
 - ✓ New MOF development for CO₂ adsorption and the modification of metal organic framework.
 - ✓ Use of renewable biochar sorbents for CO₂ capture and the modification of biochar to enhance CO₂ capture capacity and the tolerance of pollutants in CO₂ sources.
 - ✓ In the end, the report provides economic analysis of CO₂ absorption, CO₂ adsorption, and membrane separation.
 - ✓ Recent technology developments for membrane-based CO₂ capture related to the development of new membranes.
 - ✓ Recent developments on other CO₂ capture technologies including pre-combustion CO₂ capture oxyfuel combustion, chemical looping, and cryogenic carbon capture.
 - ✓ Technology assessment and report the hurdles of the development of CO₂ capture technologies.

SCOPE OF REPORT

- In this report delivered in September 2022 to members of **TCGR's Carbon Dioxide Capture and Conversion (CO₂CC) Program**, recent developments related to CO₂ capture technologies, in particular absorption using liquid solvents, adsorption using solid adsorbents, and advanced membrane-based CO₂ separation are evaluated and discussed.
- The scope covers materials development, reaction mechanisms, the optimization of process parameters, reactors design, system integration, economic performance, the innovative configuration of system units, etc. In addition, other CO₂ capture technologies, including oxyfuel combustion, chemical looping, direct air capture (DAC), and cryogenic carbon capture are covered in this report.
- **Chapter 1** discusses the background behind climate change and introduces the concept of carbon capture, storage, and utilization (CCUS) for decarbonization of energy and industrial sectors, while also noting some recent policy achievements.
- **Chapter 2** covers 'Materials for Post-combustion and Pre-combustion CO₂ Capture', discussing different solvents including strong and weak alkaline as well as aqueous amine solutions. This chapter also includes an economic analysis, which highlights the different measures of carbon capture cost.
- **Chapter 3** covers 'Materials for CO₂ Capture by Adsorption Methods' and introduces the different and common adsorbents that exist in the field. The chapter covers mesoporous, MgO-, CaO- and biochar-based materials as well as metal organic frameworks (MOFs).
- **Chapter 4** covers 'Materials for CO₂ Separation by Membrane Technology' and discusses CO₂/N₂ separation from flue gases, CO₂/H₂ separation in syngas processing, and CO₂/CH₄ separation in natural gas and biogas sweetening. An overview of current pilot plant results are also included.
- **Chapter 5** covers 'Other CO₂ Capture and Separation Technologies,' including discussions on oxy-fuel combustion carbon capture, chemical looping, DAC, and cryogenic carbon capture.

MATERIALS FOR POST-COMBUSTION AND PRE-COMBUSTION CO₂ CAPTURE: SYNGAS PRODUCTION

- Removing carbon before the combustion of carbonaceous fuels is an important method of reducing CO₂ emissions. Hydrogen production plays a key role in this pre-combustion CO₂ capture. Due to the availability and related infrastructure, a large amount of research has been carried out in relation to steam methane reforming (SMR). Homogeneous heat distribution in the steam reformer is one of the key challenges.
- In addition, a new 3D particle-resolved CFD (computational fluid dynamics) model has been successfully developed to simulate a cylindrical electrically insulated tube reactor for SMR and calculate the 3D distribution of electric field inside the reformer considering the intraparticle heat and mass transfer.
- Catalysts are essential for SMR and have been extensively researched. The active sites of SMR catalysts include Ni, Co, Cu, Mo, Au, Pt, Pd, Rh, etc., which could be classified as non-noble and noble catalysts. The most popular catalyst is Ni-based, which is low cost and catalytic efficiency. However, Ni-based catalysts have challenges of deactivation.
- Renewable feedstock has also been extensively studied for hydrogen production through steam reforming processes. Key focuses are related to catalyst development, reactor design, and process optimization, aiming to improve the production of hydrogen, the stability of the catalyst, and the overall efficiency of the process.

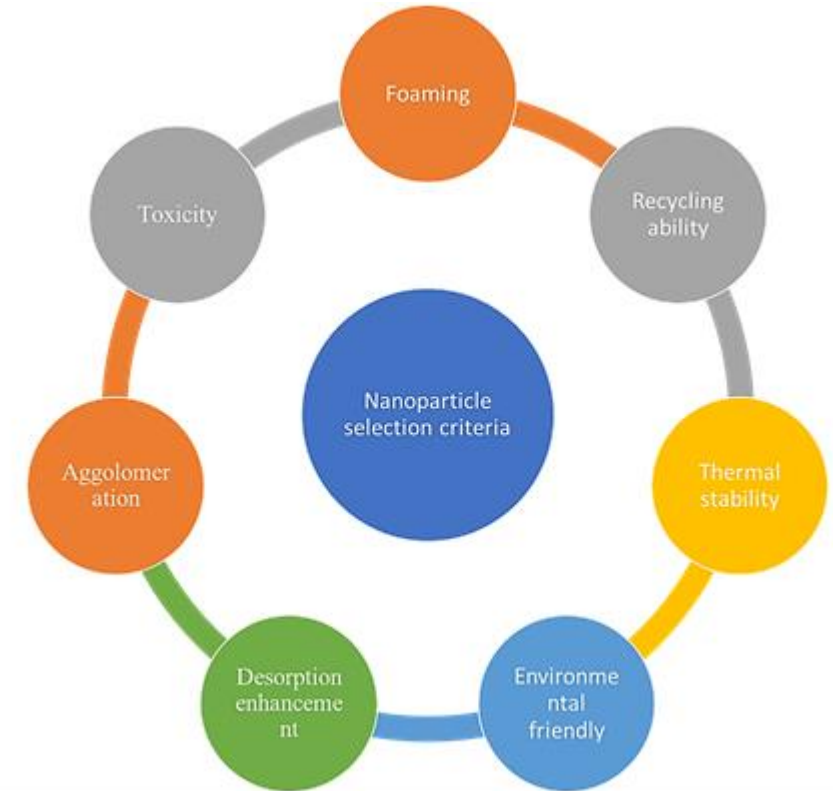


Figure 1: Nanoparticles selection criteria for solvent regeneration. Source: Mohd Rozaidin and Lau, 2022.

MATERIALS FOR CO₂ CAPTURE BY ADSORPTION

METHODS: ADSORPTION WITH MgO-BASED MATERIALS

- MgO is one of the most promising adsorbents for post-combustion CO₂ capture. It has a very high theoretical CO₂ capture capacity and is the most important medium temperature sorbent.
- Recently, extensive research has focused on modifying MgO sorbent, such as using different precursors to control the morphologies of MgO.
- Magnesium nitrate hexahydrate derived MgO showed the highest CO₂ uptake capacity. However, the stability of the produced MgO still needs to be improved.
- Alkali promoted MgO sorbents might be the most effective method to enhance CO₂ capture performance, as alkali salts can enhance CO₂ solubility.
- For example, excellent CO₂ uptake performance was obtained with 7.2 mmol/g capture capacity and stability after 50 cycles at 300 °C capture temperature after adding alkali nitrates to MgO with a molar ratio of 0.2.

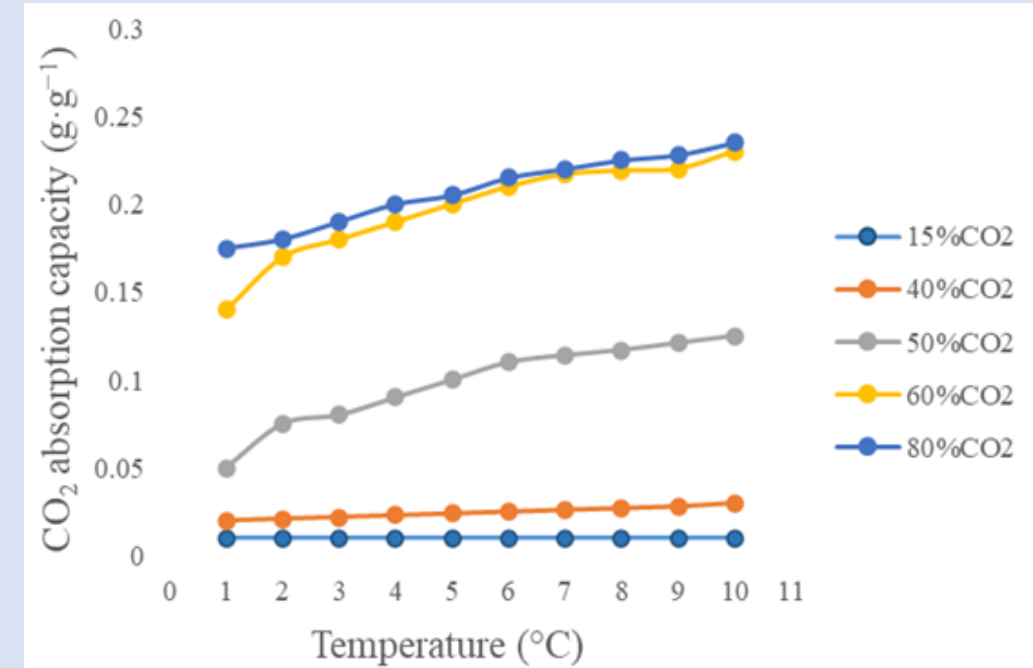


Figure 2: Influence of CO₂ concentration on CO₂ adsorption using alkali metal salt promoted MgO sorbents. Source: Chen et al., 2021.

MATERIALS FOR CO₂ SEPARATION BY MEMBRANE TECHNOLOGY

- Because of the low CO₂ partial pressure, a highly CO₂-permeable yet highly selective membrane is needed to achieve a deep carbon cleaning. In addition, since the CO₂ captured and low-purity N₂ are the byproducts, membrane process does not have the luxury of producing a high-value product to rebate its capital and operational costs.
- Compared to other purification processes, membranes are known for their system compactness, energy efficiency, operational simplicity, and ability to overcome thermodynamic limitations. Carbon dioxide separation and capture could be the next opportunity for the large-scale deployment of gas separation membranes.
- Membrane-based carbon capture is best suited for emissions from large stationary sources. Based on the location, these applications can be divided into three categories: (1) CO₂/N₂ separation from flue gases, (2) CO₂/H₂ separation in syngas processing, and (3) CO₂/CH₄ separation in natural gas and biogas sweetening.
- In comparison, in pre-combustion carbon, there is a much more favorable syngas composition of ca. 40% CO₂ and 56% H₂ with balance of water, CO, H₂S, etc., at a temperature of approximately 240°C and a pressure as high as 50 atm. The high transmembrane driving force relaxes the requirement for a highly-permeable membrane, but the membrane material needs to exhibit a high CO₂ or H₂ selectivity at a high temperature in order to reduce the H₂ loss and avoid a significant syngas cooling.
- For these CO₂ separation applications, the drastically different operating conditions also impose different challenges on the membrane material development. In CO₂/N₂ separation, the chemical properties of polymers are altered to promote the CO₂ sorption, and thus separate this gas pair that is similar in molecular size. The synthesis of CO₂-philic functional polymers is a prominent research area, for which various Lewis bases are often incorporated for their favorable physical interaction or chemical reaction with CO₂.

OTHER CO₂ CAPTURE AND SEPARATION TECHNOLOGIES: CHEMICAL LOOPING REFORMING

- Chemical looping reforming (CLR) is a promising technology for syngas and hydrogen production. It has been widely investigated for steam reforming of methane, alcohols, and glycerol.
- The results showed that the doping of Cu could enhance the reducibility of the oxygen carriers and result in the enhancement of syngas production. The oxygen carrier showed good stability after 11 cycles of CLR-SMR, and no CO was formed during 3-11 cycles, indicating the excellent resistance to carbon formation during the water splitting step.
- The feasibility of using renewable glycerol as the feedstock for syngas production was tested using CLR. It was suggested that the oxygen to glycerol molar ratio was a key parameter in controlling the composition of the produced syngas. The increased addition of water could increase the yield of syngas and H₂/CO molar ratio.
- A packed bed reactor was tested for CLR with CO₂ capture using NiO/CaAl₂O₄ as the oxygen carrier. The conversion of the feedstock and the reaction kinetics were promoted with the increase of reaction temperature.
- Recently, sorption enhanced chemical looping is gaining attention, integrating in-situ CO₂ capture into the CLR process.

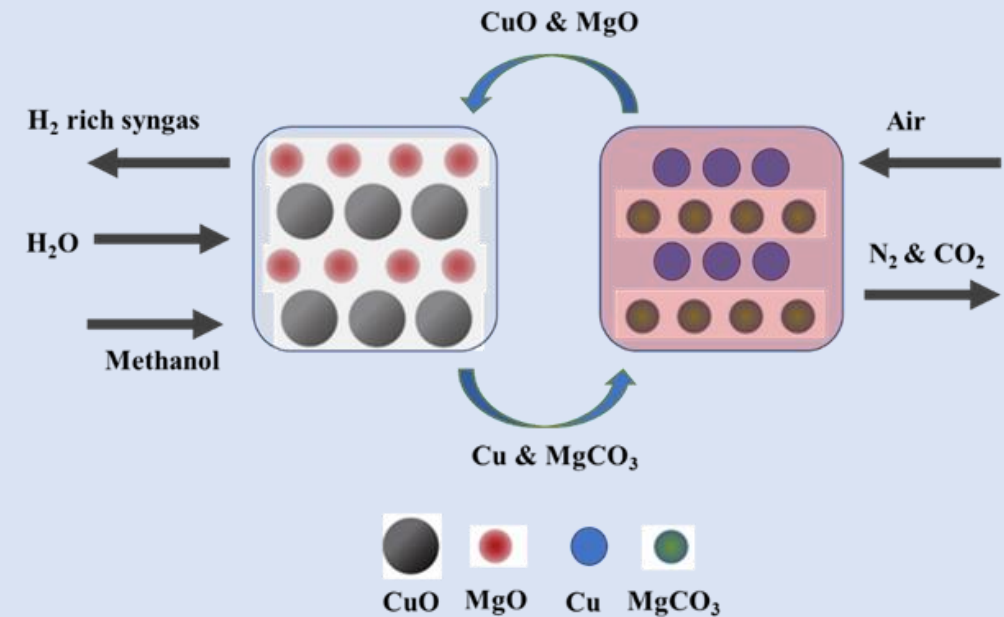


Figure 3: Schematic diagram of sorption enhanced chemical looping reforming of methanol. Source: Zeng et al., 2022

KEY TAKE-AWAYS

- Catalyst development for hydrogen production is a key challenge for pre-combustion CO₂ capture. To overcome high temperature requirement for hydrogen production, non-thermal plasma-assisted processes could be interesting, as it also favors hydrogen production from a thermodynamics perspective.
- Another key future research area for pre-combustion CO₂ capture can be related to dual or multifunctional materials development. The dual functional materials could capture CO₂ and convert the captured CO₂ simultaneously during the regeneration of materials. This technology can reduce the energy requirement, intensify CO₂ capture and utilization, and thus reduce the overall process costs.
- Silica-based materials are promising for CO₂ capture due to their controllable pore structure and high thermal stability. These materials show interesting results related to the influence of water, which is normally undesirable. The presence of water during material preparation could enhance the polymerization of SBA-15 sorbents and amine loading.
- Porous carbon is another type of solid adsorbent for CO₂ capture. Excellent CO₂ capture capacity could be achieved ascribed, to high surface area, crystallinity, and high micro- and mesopore volumes, when a novel cum graphitization method was applied through the activation using potassium acetate and iron acetate with simultaneous graphitization.
- For a higher CO₂ recovery, a multi-stage cascade design is mandatory. Enriching and stripping cascades are both suitable for 90% CO₂ recovery, provided that sophisticated recycling streams are designed in the processes to enhance the CO₂ flux. In order to achieve a >95% CO₂ purity, a CO₂/N₂ selectivity greater than 50 is needed to make the process feasible.
- The addition of amine groups to solid adsorbents has been proven to enhance CO₂ capture capacity and lower regeneration energy. However, the stability of amine grafted sorbents needs to be further studied, related to the leaching and evaporation of amine groups.

Carbon Dioxide Capture and Conversion (CO₂CC) Program



The **Carbon Dioxide Capture and Conversion (CO₂CC) Program** is a membership-directed consortium, launched in January 2010, whose members are involved in developing, monitoring and utilizing the “state-of-the-art” in technological progress and commercial implementation of industry decarbonization, including carbon dioxide capture and conversion.

The program’s objective is to document and assess technically and commercially viable options for industry decarbonization, including the capture/clean-up/utilization of CO₂ and its mitigation via energy efficiency gains which meaningfully address the challenges posed by CO₂ life-cycle and overall sustainability issues. Included in the program’s scope are:

- ☐ Global decarbonization efforts towards net zero or negative carbon emissions
- ☐ Industrial process technology shifts towards renewable, circular and sustainable practices
- ☐ CO₂ capture and/or separation
- ☐ CO₂ concentration, purification and/or other post-treatment
- ☐ CO₂ utilization/conversion (e.g., CO₂ as feedstock) for use as a fuel or intermediate, including enhanced oil recovery (EOR)
- ☐ Energy requirements (and other costs), including energy efficiency
- ☐ Industrial process improvements and energy saving initiatives which mitigate CO₂ production
- ☐ Bottom-line financial (income) impacts resulting from CO₂ reduction programs
- ☐ Life-cycle considerations and sustainability of CO₂ applications
- ☐ GHG/CO₂ regulation and “cap and trade” developments

By the direction of the member companies (through balloting and other interactive means) and operated by TCGR, the program delivers weekly monitoring communications via email (CO₂CC Communiqués), three techno-economic reports (highly referenced and peer reviewed) and scheduled meeting of members (either in-person or via webinar). **Access to deliverables is exclusive to members.**

In addition to the program deliverables, TCGR works with members to identify and foster competitive advantage and opportunity. This value-added relationship, along with active participation by membership, leads to improved (or unique) external R&D and commercial investment possibilities

Contact & More Information

More information about this and other services of the CO₂CC Program can be seen at
http://www.catalystgrp.com/php/tcgr_co2cc.php

Call +1-215-628-4447 or e-mail John Murphy, President jmurphy@catalystgrp.com,
and we'll be happy to discuss these and other interesting membership benefits

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