



## Process and engineering trends in membrane based carbon capture



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### ABSTRACT

Global warming due to greenhouse gases mostly carbon dioxide has become a serious concern worldwide. Carbon capture using adsorption, absorption, chemical looping combustion, cryogenic and membrane separations has been widely studied to tackle this problem. Significant research efforts have been made in membrane based carbon capture employable in both pre- and post-combustion options as it is a simple, efficient economical and environmentally benign option. In this paper, a comprehensive review has been done on this technology with reference to various aspects viz., synthesis, characterization and performance analysis of various membrane materials, contactors and their design aspects, modeling and simulation studies and membrane wetting phenomenon. The prospects and future challenges of the membrane based carbon capture are also highlighted.

### 1. Introduction

Carbondioxide (CO<sub>2</sub>) being one of the most harmful gases in the world, is an integral part of most of the flue gases from industries. It's rising levels in the atmosphere could be attributed to increasing industrial demands and various natural processes like volcanoes, ocean

temperature oscillations, fires, etc [1,2]. Industries play a predominant factor and contributes to nearly 40% of all CO<sub>2</sub> emissions in the world, with reports suggesting that the main contributors being the power and cement industries [3,4]. A study suggests that a 600MW coal fired power plant could generate flue gases at a rate of 500 m<sup>3</sup>/s, a significant constituent of which is CO<sub>2</sub> [5]. Concentration in the

**Abbreviations:** 1D, One Dimensional; 2D, Two Dimensional; 40MCO–60CPO, Mn<sub>1.5</sub>Co<sub>1.5</sub>O<sub>4</sub>·8–60 wt%Ce<sub>0.9</sub>Pr<sub>0.1</sub>O<sub>2</sub>·8; 60CGO–40BSCF, Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2</sub>·8–40 wt% Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>·8; 6FBPA, Hexafluorobisphenol A; 6FPYP, 2,6-bis(trifluoromethylphenylene)pyridine; 6FPT, 2,5-bis(3-trifluoromethylphenylene)thiophene; AFM, Atomic Force Microscopy; AFRC-AHLE, Aqueous free radical copolymerization followed by acid hydrolysis and ion exchange; AMP, 2-amino-2-methyl-1-propanol; APTS, (3-Aminopropyl) triethoxysilane; ATR, Attenuated total reflectance; BBL, polybenzimidazo-benzoisoquinoline; BET, Brunauer-Emmet-Teller; CaLS, Calcium lignosulfonate; CAP, Continuous Assembly of Polymers; CC, Carbon Capture; CCP, Carbon Capture Project; CCS, Carbon Capture and Sequestration; CLC, Chemical Looping Combustion; CNT, Carbon Nano Tube; DEA, Diethanolamine; DJWSP, Dry jet/wet spinning process; DMAc N NAPDE, Nonlinear Algebraic Partial Differential Equation; NELF, Non-Equilibrium Lattice Fluid; N-Dimethyl acetamide; DMAEMA-AA, dimethylaminoethyl methacrylate-acrylic acid; DME, Dimethyl ether; DNMDAm, 3,3'-Diamino-N-methyldipropylamine; DSC, Differential scanning calorimetry; EDTA, Ethylenediaminetetraacetic acid; EDS, Energy Dispersion Spectrometer; EDXS, Energy dispersive X-ray spectroscopy; EOR, Enhance Oil Recovery; ESEM, Environmental scanning electron microscope; FESEM, Field Emission Scanning Electron Microscopy; FFV, Fractional free volume; FTIR, Fourier Transform Infrared Spectroscopy; FVM, Finite Volume Method; GO, Graphene Oxide; HFPSF, Hexafluoropolysulfone; ICP, Inductive coupled plasma; IEA, International Energy Agency; IR, Infra-Red; KJS, Kruk-Jaronaic-Sayari; Ksar, Potassium sarcosinate; LBLST-SGC, Layer-by layer seeding technique followed by secondary growth crystallization; LEP, Liquid Entry Pressure; LOMOMS, Layering of membrane on mullite support; MDEA, Methyl diethanolamine; MEA, Monoethanolamine; MIP, Mercury Intrusion Porosimetry; MMM, Mixed Matrix Membranes; MS-U, Mass Transfer based UNIQUAC; MNWT, Multi-walled nanotubes; MWCNT, Multiwall Carbon Nanotubes; NF/RO, Nano filtration/Reverse Osmosis; NMP, N-Methyl-2-pyrrolidone; P (DAD- MACA-co-VAm), Poly (diallyldimethylammonium carbonate-co-vinylamine); PAMAM, Poly(amidoamine); PANI, Polyaniline; PBI, Polybenzimidazole; PBI, Polybenzimidazole; PDMAEMA, poly (N, N-dimethylaminoethyl methacrylate); PDMS, Poly (dimethyl siloxane); PDU, Process development unit; PE, Polyethylene; Pebax, Polyether block amide; PEDOT, Poly(3,4-ethylenedioxythiophene); PEG, Polyethylene glycol; PEGDA, Polyethylene (glycol) Diacrylate; PEGDMA, PEG dimethacrylates; PEGDME, Poly (ethylene glycol) dimethyl ether; PEI, Polyetherimide; PEO, Poly ethylene oxide; PFA, Polyfluoroaniline; PIL, Polymeric Ionic Liquid; PIM, Porous Intrinsic Membrane; PPG, Polypropylene glycol; PSA, Pressure Swing Adsorption; PSF, Polysulfone; PSS, Polystyrene sulfonate; PTFE, Poly(tetrafluoroethylene); PVA, Poly (vinyl alcohol); PVDF, Polyvinylidene fluoride; QSPR, Quantitative Structure Property Relationship; RF, Radio frequency; RO, Reverse Osmosis; RTIL, Room Temperature Ionic Liquid; SCFR, Semi continuous flow reactor; SDA, Structure-directing agent; SEM, Scanning electron microscopy; SILM, Supported Ionic Liquid Membrane; SLM, Supported Liquid Membranes; SMM, Surface Modifying Macromolecules; STEM, Scanning transmission electron microscopy; TAB, 1,3,5-triaminophenoxybenzene; TEM, Transmission electron microscopy; TFC, Thin Film Composite; TFE, Tetrafluoroethylene; TGA, Thermal gravimetric analysis; TMC, trimethylsilyl chloride; TMF, Tetrahydrofuran; TMHFPC, Tetramethylhexafluorocarbonate; TMMPD, Trimethyl-w-phenylenediamine; TR, Thermally Rearranged; TRIS, 3-[Tris(trimethylsilyloxy)silyl] propyl acrylate; TSA, Temperature Swing Adsorption; TTD, 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole; UTFC, Ultra-thin film composite; UV SPEC, Ultra violet spectroscopy; WGS, Water Gas Shift; WGSMT, Water-gas shift membrane reactor XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffractometer; XRF, X-ray fluorescent spectroscopy; ZA, Zinc Acetate; ZC, Zinc Chloride; ZN, Zinc Nitrate

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**Nomenclature**

$P_A$	Permeability
$D_A$	Diffusivity
$S_A$	Sorption Coefficient
$T$	Temperature
$\Delta p$	Pressure gradient
$\eta$	CO <sub>2</sub> capture ratio
$K_{ov}$	Overall mass transfer coefficient
$u_g$	Interstitial gas velocity
$A$	Specific interfacial area
$C_{CO_2,l}$	Concentration of CO <sub>2</sub> in liquid phase
$C_{CO_2,g}$	Concentration of CO <sub>2</sub> in gas phase
$Q_g$	Flow rate of gas phase
$K$	local mass transfer coefficient
$S_{Shell}$	Module area without fibers
$y_{co_2}$	Volume fraction of CO <sub>2</sub> in gas phase
$P_g$	Gas phase pressure
$Q_l$	Flow rate of liquid phase
$C_{MEA, l}$	Concentration of MEA in liquid phase
$u_{z,l}$	Liquid velocity at coordinate z
$r$	Radial coordinate

$D_1$	Coefficient of diffusion of CO <sub>2</sub> in liquid phase
$D_{MEA}$	Diffusion coefficient of MEA in liquid phase
$R_{CO_2}$	Reaction rate of CO <sub>2</sub> with MEA
$u_{z,g}$	Gas velocity at coordinate z
$D_{meff}$	Effective CO <sub>2</sub> diffusion in membrane
$S^\infty$	Infinite dilution solubility coefficient
$\alpha_{CO_2/CH_4}$	Selectivity of CO <sub>2</sub> /CH <sub>4</sub>
$\alpha_{CO_2/N_2}$	Selectivity of CO <sub>2</sub> /N <sub>2</sub>
$\beta$	Pore geometry coefficient
$\gamma$	Liquid surface tension
$\theta$	Contact angle
$d_{max}$	Maximum pore diameter
$P$	Permeance
$\Delta p$	Pressure difference across membrane;

**Unit conversions**

1 Barrer	$3.348 \times 10^{-19}$ kmol m/(m <sup>2</sup> s Pa)
1 GPU	$10^{-6}$ cm <sup>3</sup> (STP)/cm <sup>2</sup> s (cm Hg)
1 psig/psia	6894.76 Pa
1 atm	101325 Pa

atmosphere was just 280 ppm before the industrial era [6–9] and has reached its all-time high of 400 ppm in 2015 [10]. With no alternative in sight for fossil fuels and the demand for energy only increasing, we could expect this number to reach catastrophic limits soon. Moreover, the associated global temperature increase due to CO<sub>2</sub> emissions is projected to be somewhere between 1.4 to 5.8 °C by the start of the 22nd century [9], unless climate change policies are properly implemented. Thus, this level of rising CO<sub>2</sub> concentration may lead to catastrophic events and ecological imbalance [11].

To reduce the CO<sub>2</sub> emissions, three options available are reducing energy intensity, reducing carbon footprint and improving carbon capture and sequestration (CCS). First one requires an efficient use of energy which could be accomplished by reducing energy penalties in different industries while the second option requires finding alternatives to fossil fuels viz., wind energy, solar energy, tidal energy etc. Third option requires exploration of new methods of CO<sub>2</sub> capture and storage. With no possibility of large scale replacement of fossil fuels with alternate ones in the near future, CCS seems to be the only option for mitigating CO<sub>2</sub> emissions. Storage of CO<sub>2</sub> could be done in deep geological or oceanic sites [12–16], which reduces the chances of anthropogenic CO<sub>2</sub> emissions [17]. Alternatively, the captured CO<sub>2</sub> could also be used in many applications, viz., food and metal industries, EOR, chemical feedstock and solvent extraction [18–22]. Thus CC is the best solution available today to tackle rising CO<sub>2</sub> emissions. The practical application of CC technology in the boundary dam, Saskpower, Canada in 2014, [23], has not only reinforced this but has also led to fostering of research in this field.

CC could be broadly classified as post-, pre- and oxy-fuel combustion types. The process of removal of CO<sub>2</sub> depends on the type of combustion process used. It involves additional infrastructure requirement and energy penalty [24], and hence is an option only in large scale plants where the process could be economically viable. In post combustion method, CO<sub>2</sub> is removed from the flue gases after the fuel combustion. It is hence compatible with the existing power plants and requires only slight modifications. However, the energy penalty involved in this type of capture is large, as the concentration of CO<sub>2</sub> in flue gases is quite low [25–27]. Furthermore, though the concentration of CO<sub>2</sub> in these flue gases, varies owing to factors like fuel and process used, the gas is almost always present with a significant amount of SO<sub>2</sub>, NO<sub>2</sub> and other constituents. Thus the energy penalty though varying with the process is always present. In contrast, in the pre-combustion

method, the fuel goes through a process which eases the separation of CO<sub>2</sub> later. For example, gasification process is carried out so that fuels like natural gas are directly converted to syn-gas using reforming. Detailed studies are reported on the efficiency and cost analysis of CC in this case [28]. Oxy-fuel combustion uses pure oxygen instead of air, thereby lowers the concentration of NO<sub>x</sub> formed. Hence flue gases in this case mainly consist of only water vapour, particulate matter, CO<sub>2</sub> and SO<sub>2</sub> [29]. The major drawback of this method however is the need of separation of O<sub>2</sub> from atmosphere for generating pure oxygen [30]. Also, since reduction of other gases, increases the concentration of SO<sub>2</sub>, corrosion becomes a major issue. A recent study by IEA, projected that the proper implementation of CCP would lead to a 14% drop in the man-made greenhouse gas emissions [31].

There are several techniques available for the separation of CO<sub>2</sub> from flue gases, the most prominent ones being absorption, adsorption, CLC, cryogenic distillation and membrane separation.

Absorption involves the use of a liquid sorbent to separate CO<sub>2</sub> from flue gases. Later, the sorbent is recovered by stripping, heating or depressurization. This process has received a lot of attention from researchers and is the most developed technology till date [1,32–34]. Due to the extensive research done on this area, lot of sorbents are readily available today that suit most of the industrial scenarios [35]. The major drawback in absorption technique is the solvent loss due to amine degradation, which in turn produces volatile degrading compounds [36,37]. As an alternative, adsorption could be used as a viable method, where a solid sorbent is used instead for the CO<sub>2</sub> separation. The sorbent selection here is based on high surface area, high selectivity and high regeneration ability. CO<sub>2</sub> is later recovered from the sorbent by changing the temperature (TSA) [38,39] or pressure (PSA) [40–42]. PSA has shown an efficiency of 85% at a commercial scale recovery [43]. The scale of research done in this method is slowly increasing and search for novel sorbents from industrial and agricultural wastes is grabbing worldwide attention [44–47]. CLC is similar to oxy-fuel combustion but it uses an oxygen carrier like metal oxides for transferring oxygen from air to fuel. In the phase I of the CC project (CCP), CLC was reported to be one of the best alternatives for cost reduction [48]. The process involves two stages, i.e., oxidation and reduction. Initially, metal oxide gets reduced during the fuel combustion which is regenerated by oxidation in the presence of air. The main advantage of this method is that it generates a mixture of CO<sub>2</sub> and H<sub>2</sub>O from which CO<sub>2</sub> could be easily separated by condensing water. Studies

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