A journey into the process and engineering aspects of carbon capture technologies

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ABSTRACT

Atmospheric warming due to greenhouse gases has become a serious global concern. Extensive efforts are being made to combat this phenomenon through Carbon Capture as carbon dioxide is its major contributor. In this work, a comprehensive review has been made on various Carbon Capture methodologies including adsorption, absorption, membrane separation, Chemical Looping Combustion, cryogenic separation with focus on their process chemistry, critical process parameters, contactor configurations, kinetics, thermodynamics, process development and scale-up. The challenges at the research and development stages have also been identified so as to provide the future directions for research.

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Abbreviations: AAP, agglomeration and attrition of particles; A,a, adsorption cycle; AplF, application formulated; APOC, analytical proof of concept; AR, air reactor; ARR, auto reduction reactor; BESs, bioelectrochemical systems; BFB, batch fluidized bed; BN, boron nitride; BPOB, basic principles observed; BR-MPBR, biomass retention-membrane photo bio reactor; BS, bench scale; BZx, binderless zeolite 13X; CASU, cryogenic air separation unit; CASU-PB, cryogenic air separation unit-packed bed; CC, CO2 capture; CCl, combined cycles integrated; CDCL, coal direct chemical looping; CLAS, chemical-looping air separation; CLC, chemical looping combustion; CLOU, chemical-looping with oxygen uncoupling; CLP, calcium looping process; CMBS, circulating moving bed system; C-MPBR, carbonation-membrane photo bio reactor; CoC, counter current; CnC-MBR, counter-current moving bed reactors; Con-O, continuous operation; CPDM, component prototype demonstration; CPO, component prototype development; CRS, condensed rotational separation; D, desorption cycle; DOCPB, dynamically operated cryogenic packed-bed; ESA, electric swing adsorption; FAC, fine activated carbon; FBR, fluidized bed reactor; FFeed, feed inlet conditions; FPS, free piston stirling cooler; FR, fuel reactor; FRR, fiber to resin ratio; FSCD, full-scale commercial deployment; GP, gas permeation; HCM, honeycomb monolith; HTC, hydro talsite; ICC, inlet CO2 concentration; IFBR, interconnected fluidized-bed reactors; IPA, isopropanol amine; Lx, liquid flow area; LCT, laboratory component testing; LS, lab scale; MBA, moving bed adsorber; MCFC, molten carbonate fuel cells; MCR, max. compression ratio (per stage); MEA, methyl ethyl amine; MECs, microbical electrolysis cells; MEDC, microbial electrochemical cell; MOF, metal oxide framework; MS, microwave synthesis; MOx, oxidized form of metal oxide; MoO3-x, reduced form of metal oxide; N, absorption rate; NDC, non-dispersive contact; NPCIO, nitrogen enriched porous carbons; OC, oxygen carrier; OFC-I, 1st generation oxy-fuel combustion; OFC-II, 2nd generation oxy-fuel combustion; OFC-III, 3rd generation oxy-fuel combustion; PBR, packed-bed reactor; PEG, poly ethylene glycol; PEL, poly ethylene imine; Pex, product exit conditions; Post-CCC, post-combustion CC; PP, partial pressures; Pre-CCC, pre-combustion CC; PSA, pressure swing adsorption; PSD, pilot scale demonstration; RPBR, rotary packed bed reactor; SABF, sound assisted fluidized bed; SC, semi continuous; SLM, supportive liquid membranes; S-P, selectivity and permeability; SPM, substituted polymer membranes; SSDC, sub-scale commercial demonstration; STCR, steam to carbon ratio; STS, solvothermal synthesis; TSA, temperature swing adsorption; VPSA, vacuum pressure swing adsorption; ZIF, zeolitic imidazolate frameworks; ZX, zeolite 13X

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1. Introduction

The first meeting of United Nations Framework Convention on Climate Change (UNFCCC) held in 1992 had triggered for global concern on climate change due to GHG emissions. The global warming due to carbon dioxide emissions has been receiving worldwide attention to mitigate its adverse effect on the climate in terms of temperature rise, continuous rise in sea level, increasing occurrence of storms and floods. The main focus is on developing novel processes for carbon dioxide capture (CC) [1–4]. It has been predicted by the International Panel of Climate Change (IPCC) that by the year 2100, the atmospheric content of CO2 shall reach 570 ppmv, rise in sea level of 3.8 m and a rise in global mean temperature of about 2°C with very serious consequences on environment [5–8]. Coal continues to be the main fuel for power generation worldwide and hence integrating CC with power generation through pre and/or post-combustion options is on the main agenda [9,10].

The relationship between the CO2 emissions (CD) with the population (P), economic development (represented by gross domestic product, GDP), energy production (E), carbon based fuels used for energy production (C) and CO2 sinks (SCO2), expressed by the modified Kaya’s identity [11]:

\[
CD = \frac{P \cdot GDP \cdot E \cdot C}{GDP \cdot E \cdot SCO2}
\]  

(1)

It shows that the three feasible ways to reduce the CO2 emissions viz., increase of energy efficiency (E/GDP), change of the fossil fuels to non-carbon forms of energy (for e.g., renewable and nuclear energy) and to create CO2 sinks with the help of CC technology [12,13]. It can be achieved through technological options like pre-combustion removal of CO2 from the fuel, post-combustion removal of CO2 from the flue gases, oxyfuel combustion (OFC) to provide CO2 at a high concentration in the flue gases, chemical looping and clathrate hydrate processes [14–16]. The presence of CO2 at a relatively higher concentration and at a higher pressure in a pre-combustion option make them economically, thermodynamically and kinetically more attractive. Post-combustion CC though expensive is advantageous in that it can be successfully integrated to the existing power generation plants to enhance their efficiency with simultaneous CC. Oxyfuel combustion (OFC) CC is the latest of all technologies and is yet to be commercialized. By employing pure oxygen, the undesirable gases like NOx are minimized and CO2 concentration is enhanced. It can be operated at high pressures reducing the cost of CC. It, however, suffers from drawbacks like the need for expensive cryogenic air separation unit, higher material requirement and high temperatures for handling flue gases and their recirculation [17–19].

The post-combustion options for the CC are adsorption, absorption (physical and chemical), membrane and cryogenic separations (Fig. 2). Absorption based CC employs physical or chemical interactions between the CO2 and the absorbent. Solvents like rectisol, selexol... etc. are employed for physical absorption [14]. For chemical absorption, solvents like amines, alcohols and their compatible blends, liquid ammonia and alkalies like NaOH, K2CO3, and Na2CO3 are employed. Chemical absorption is widely employed due to higher capture efficiencies even at low concentrations of CO2 and higher selectivity's [20–26]. Adsorption attaches gas or liquid on solid adsorbents which then could be regenerated by the application of temperature swing, pressure or vacuum swing. Adsorbents like activated carbon, alumina, metal oxides, zeolites and phosphates [14,27–30], metal organic frameworks [31–34], microporous carbons and polymers [35–39] and modified amines [40–42] are employed. CC could also be achieved through membranes separation of CO2 from flue gases constituents due to its difference in permeability and selectivity. Organic (polymeric) and inorganic (ceramic, carbon, zeolite, metallic, etc.) membranes are employed for separation. Membrane also acts as a contacting device for the gas and the solvent moving in counter-current fashion with CO2 getting selectively absorbed on the membrane matrix [15,43,44]. The advantages of the membrane technology are high product purity, low cost, continuous processing with very low start up time while the disadvantages could be non-attractiveness at low CO2 concentrations and high flue gas temperatures and membrane fouling. Novel and effective membranes can be developed by incorporating functional groups like amines, combination of different and compatible membrane materials and manufacture of biomimetic configurations [45–47].

The fourth technical option of CC is cryogenic separation involving the compression and cooling of gas mixture with CO2 at various levels to facilitate phase change of the CO2 along with other constituents which can then be separated using distillation. The advantages of this process are that no chemical absorber is needed, can be operated at atmospheric pressure and its compatibility with both pre- and oxy-combustion CC with easy transport of liquid CO2 formed. Its drawbacks are its feasibility at high CO2 concentrations (> 50%), formation of ice or solid CO2 clathrates in the presence of water vapor leading to serious plugging, pressure...
build-up issues and reduction of heat transfer rates due to thick CO₂ layers formed on heat exchange surfaces [14–16]. CLC is the advanced version of OFC where the necessary oxygen for the combustion is released by the oxygen carrier in gaseous phase thereby eliminating the gasification step while employing gaseous fuels and also requiring smaller reactors reducing capital costs when compared to CLC. This technology requires further research before commercialization [50,51]. The Technology Readiness Levels (TRLs) of all the above mentioned CC technologies are highlighted in Table 1 [5,6].

Table 1 shows that except gasification, oxyfuel combustion and CO₂ capture by absorption, other technological options need R&D

Table 1  TRL’s of CC technologies.

<table>
<thead>
<tr>
<th>TRL</th>
<th>Scope</th>
<th>Time (years)</th>
<th>Pre-Combustion</th>
<th>Post-Combustion</th>
<th>Pre- &amp; Post-Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gasification</td>
<td>IGCC</td>
<td>Abs.</td>
</tr>
<tr>
<td>9</td>
<td>FSCD</td>
<td>3–6</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>8</td>
<td>SSSCD</td>
<td>2–5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>7</td>
<td>PDD</td>
<td>2–5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>6</td>
<td>CPDm</td>
<td>2–4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>5</td>
<td>CPDT</td>
<td>–</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>4</td>
<td>LCT</td>
<td>–</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>3</td>
<td>APOC</td>
<td>–</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>2</td>
<td>APLF</td>
<td>–</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>1</td>
<td>BPOB</td>
<td>–</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

M_{\text{CO}_2} mole fraction of CO₂  
M_{\text{FGas}} mass of flue gas (g/g of CO₂)  
m_t mass flux of CO₂ deposition from flue gas to the surface of cooling fin  
P pressure (MPa)  
P_{\text{V}} pore volume (cm³/g)  
P_{\text{p}} vacuum pressure (Pa)  
r_{\text{inst}} instantaneous rate of conversion of the char  
S solvent flow rate (kgh)  
S_{\text{A}} surface area of adsorbent (m²/g)  
SFRR syngas feed rate to the reducer (L/min)  
SITC steam injection to combustor (g/min)  
SPECCA specific primary energy consumption for CO₂ avoided (kJHV/kg_{\text{CO}_2})  
SPL sound pressure level (dB)  
S_{\text{i}} synthesis time (h)  
T temperature (°C)  
T_{\text{ads}} adsorption time (s)  
T_{\text{des}} desorption time (s)  
T_{\text{i}} microwave synthesis time (h)  
T_{\text{p}} repressurization time (sec)  
T_{\text{s}} solvothermal synthesis time (h)  
U_{\text{fuel}} feed velocity (m/s)  
U_{\text{inf}} minimum fluidization velocity (m/s)  
V_{\text{CH}_4} flow rate (kmol/h)  
V_{\text{f}} fluidization velocity (cm/s)  
V_{\text{gas}} flow rate (m/s)  
V_{\text{O}_{2} H_{2}O} flow rate (kmol/h)  
V_{\text{vis}} viscosity of liquid  
W_{\text{C}} adsorbent working capacity (mol/kg adsorbent/cycle)  
X_{\text{OC}} chemical conversion of oxygen carriers (%)  
X_{\text{p}} plate thickness (m)  
α_{\text{p}} gas to solid heat transfer coefficient  
Δ_{\text{H}} enthalpy of reaction  
ΔP_{\text{RC}} pressure drop across the recycle chamber  
ε porous volume fraction  
λ_{\text{eff}} effective axial heat dispersion coefficient  
ϕ OC/fuel ratio  

Nomenclature

A absorbent concentration (kmol/m³)  
(A1L1T1 for NaOH & A2L2T2: for MEA)  
AC absorbent capacity (kg/kg)  
Ad-C adsorbent capacity (kg_{\text{CO}_2}/kg_{\text{ads}})  
AT activation temperature (°C)  
B_d bulk density (g/cm³)  
C CO₂ concentration (v/v%)  
Cₚₘ cycle periods (s)  
C_s specific heat of solids (J/(g K))  
CT carbonization temperature (°C)  
D_{\text{ax}} axial mass dispersion coefficient  
D_{\text{bed}} diameter of bed (m)  
D_{\text{p}} particle size (µm)  
D_{\text{pg}} size of spherical glass particles (mm)  
D_{\text{T}} duration time (h)  
E_f enhancer flow (L/min)  
F_f fuel flow (kg/h)  
F_i inlet fuel (vol%)  
F_{\text{ solids}} flow rate of solids (g/s)  
F_T flue temperature (°C)  
G absorbent flow (m³/m² h)  
G_{\text{a}} gas flow area  
GTCC (%T/C(sensitivity efficiency))/%pump (%)  
HCC higher cyclic capacity (%)  
HCE higher cyclic efficiency (%)  
HCL higher cyclic load (%)  
HEX heat exchanger efficiency (%)  
HR heat recovery (%)  
I_{\text{C}} cell current density (A/m²)  
ICC inlet CO₂ concentration (%CO₂)  
K_{\text{C}} a_v volumetric overall mass transfer coefficient (kmol m⁻³ h⁻¹ kPa⁻¹)  
K_s thermal conductivity of solids (J/(m K s))  
L liquid flow rate (m³/m² h)  
L_{\text{bed}} length of bed (m)  
L_{\text{g}} inlet gas flow rate (L/min)  
M_{\text{E}} mole fraction of CO₂  
M_{\text{FGas}} mass of flue gas (g/g of CO₂)  
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ΔP_{\text{RC}} pressure drop across the recycle chamber  
ε porous volume fraction  
λ_{\text{eff}} effective axial heat dispersion coefficient  
ϕ OC/fuel ratio
efforts on larger scale to prove their techno-economic viability. TRL-4 is a typical end-point of R&D efforts at university level.

2. Potential pre- and post-combustion CC options

Fig. 1 shows the critical unit processes and operations involved in pre and post-combustion CC technologies and their downstream applications in thermal power and fertilizer sectors. It shows that both pre and post-combustion options can be employed for coal and biomass. Gasification and reforming of fuels can be used for achieving enhanced combustion rate and for hydrogen production. Insitu ammonia and urea production will minimize the energy penalties associated with CC [52]. The oxyfuel combustion can be implemented in three modes and two of them facilitate fuel combustion through a looping process. The current status of the above technologies can be summarized as:

- In pre-combustion technologies, the carbon in the fuel is converted into synthesis gas up to 90% before combustion through gasification or reforming processes. Employing integrated coal gasification combined cycle (IGCC) concept, the resulting gas can be further converted into a stream of H2 and CO2 through a shift reaction. The pre-combustion technologies can be applied to new power plants, their technologies are yet to reach commercial maturity levels and they require high capital investments due to major changes to be brought into boiler and flue gas systems.

- In post-combustion technologies, CO2 is separated from combustion flue gases by employing absorption, adsorption, membrane separation and other options for coal, gas, and other fossil fuel based thermal power plants by retrofitting. They are yet to be commercially established except in the case of the absorption option. The CO2 in the flue gases is in fairly diluted concentrations (10–15%) needing high recovery and capital costs and 25–30% additional energy for plant operation.

- Oxyfuel, chemical looping and clatherate hydrate processes can be employed in pre and post-combustion modes. The former employs pure or enriched oxygen for combustion of fuel or flue gases to obtain CO2 in higher concentration. The clatherate process forms hydrate crystals from water and CO2, N2, O2, H2 and natural gas components. The process enables the maximum CO2 recovery of 42.5% at 8.5 MPa [53].

In all above options for CO2 capture and recovery, pilot experimentation, modeling, validation tests and field scale demonstrations are essential to establish their commercial viability.

Post-combustion CC processes are well-suited for retrofitting into coal/gas fired thermal power plants for CO2 removal from the flue gases. They generally contain less than 15% of CO2 and smaller concentrations of nitrogen, water vapor, SOx, and NOx. Fig. 2 shows a variety CC options based on gas–liquid absorption, gas–solid adsorption and solid membrane facilitated separations. The main factors impacting CC efficiencies are flue gas composition and its temperature and energy penalties associated with the desorption process.

2.1. Gas–liquid absorption

CC by absorption is a more widely employed technical option than the other post-combustion CC options. It is a well-established phenomenon which can be easily integrated/retrofitted to any power generation system as an end of the pipe technology. Moreover, it is highly selective with very high CC efficiency. Most of the absorbents are very economical and can be easily regenerated. It has been widely used in coal gasification, petroleum refining, syn-gas production, natural gas (sweetening) and hydrogen manufacture. The literature reports show that this technology was the only commercially attractive option for CC until 2030 [54–56]. Lower efficiencies besides limited understanding of their absorption process have made them relatively less popular [7,8].

Fig. 1. Pre and post-combustion of CC technologies.
The energy penalty for CO₂ absorption–desorption lies in the range of 0.37–0.5 MWh/ton CO₂. By employing more novel solvents and their blends the energy penalty may be brought down to 0.19–0.2 MWh/ton CO₂.

Chemical absorption can effectively remove acid gases from flue gas by employing amine based solvents [10]. A reversible reaction takes place during chemical absorption forming a weakly bonded intermediate such that the reaction could be reversed by the application of heat or pressure. Also, chemical absorption gives a pure stream of CO₂ after stripping the solvent [11]. Physical absorption obeys Henry's law (temperature and pressure dependent). Organic solvents like selexol, rectisol, etc. were employed to physically absorb CO₂ at higher pressure and lower temperature which were regenerated later at reduced pressure and high temperature [12]. Fig. 3 below shows the components of an absorption system along with its type of contactors and solvents employed.

2.1.1. Absorbent selection

An absorbent should have high reactivity and absorptivity with respect to CO₂, low vapor pressure, easy regenerability, high thermal and chemical degradation stability, low environmental impact (green) and economical. Table 2 highlights the absorbent and process options. Among various absorbents used for CC the earliest and most commonly employed agent has been monoethanolamine (MEA). It is relatively cheap, has high reactivity and higher absorption rate. It can, however, degrade in oxidizing atmosphere, energy intensive during regeneration, has limited CO₂ loading capacity and corrosive with foaming and fouling characteristics [13,43,57–64]. Other alkanolamines like DEA have also been used for absorption but they also suffer from similar drawbacks. A blend of MEA and DEA i.e. Methyldiethanolamine (MDEA) has been employed with some success with improved CO₂ loading capacity, corrosion resistance, degradation and reduced regeneration costs but with lower absorption rates [54,65–69]. Diisopropanolamine (DIPA) has also been used due to its high corrosion resistances and lower regeneration costs though with similar drawbacks [59,61,70]. Sterically hindered amines like AMP (2-amino-2-methyl-1-propanol) have been tried for CC since they have high absorption capacity, higher selectivity, corrosion and degradation resistances, easy regenerability though with low absorption [64,71–74]. Aqueous blends of AMP with DEA and DIPA with MDEA are also reported [75,76].

Piperazine (PZ)/cyclic diamines have been employed due to their high loading capacity, low regeneration costs and high resistance to corrosion and oxidative and thermal degradation. PZ is more successful as a promoter due to its rapid formation of carbamates with CO₂. It was employed with MEA, diethylenetriamine (DETA), and with AMP at various ratios. AMP-PZ blend is reported to be
Table 2
Summary of absorption based carbon capture.

<table>
<thead>
<tr>
<th>Type</th>
<th>Absorbent</th>
<th>Reactive separator</th>
<th>Operating conditions P.T.C.G</th>
<th>CO₂ capture (%)</th>
<th>AC (kg/kg)</th>
<th>Kinetics/mass transfer</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single solvent</td>
<td>Ammonia</td>
<td>Sieve plate (CC)</td>
<td>T:25–55 °C C:10–14</td>
<td>95–99, 1.2</td>
<td></td>
<td>$2NH_3(g) + CO_2(g) = NH_2.COONH_4(s)+NH_2.COONH_4(s)$ (exo-endothermic)</td>
<td>Temperature curve has a peak</td>
<td>[161] [162]</td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>Spray (CC; pilot)</td>
<td>P:0.1; T:20–50 C:1–7 G:3–7</td>
<td>10–20, NA</td>
<td></td>
<td>$K_C_{CO_2} = \frac{C_{CO_2}}{C_{CO_2}^0} (1 - Y_2)$</td>
<td>$K_C\Delta_n = 0.17$, increases with G and L/G</td>
<td>[163]</td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>Flow (SC)</td>
<td>T:10–40; C:8–16; G:2–10</td>
<td>94, 0.4</td>
<td></td>
<td>$C_2H_4OHNH_2CO_2 + CO_2 + H_2O \rightarrow C_2H_4OHNH_2CO_2 + HCO_3Na$</td>
<td>NH₃ regeneration heat &gt; MEA</td>
<td>[161]</td>
</tr>
<tr>
<td></td>
<td>Spray &amp; packed</td>
<td>(CC, pilot)</td>
<td>T:25 A:3–7 G:10.3</td>
<td>100, 0–0.45 mol/mol</td>
<td></td>
<td>$K_C_{CO_2} = \frac{C_{CO_2}}{C_{CO_2}^0} (1 - Y_2)$</td>
<td>Spray column offers superior CO₂ capture</td>
<td>[164] [13] [43]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tray (simulated</td>
<td>P:0.1; T:15.2; A:30 (w/w);</td>
<td>&gt; 95, NA</td>
<td></td>
<td></td>
<td>Promising promoter</td>
<td>[103]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CC; pilot)</td>
<td>G:0.1 mol/s</td>
<td></td>
<td></td>
<td></td>
<td>Theoretical study</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MEA</td>
<td>Fixed-bed (Con-O,</td>
<td>T:60 G:40 ml/min</td>
<td>99.4, NA</td>
<td></td>
<td>$N = C_D^1 V_D k_2 C_{CO_2}^0$; pseudo-1st order reaction</td>
<td>Reactivity decreases at 40–200 °C</td>
<td>[182] [79]–[102]</td>
</tr>
<tr>
<td></td>
<td>Piperazine</td>
<td>Stirred cell (SC, BS)</td>
<td>T:42 P:0.032 &amp; 0.042</td>
<td>~100, 0.32</td>
<td></td>
<td>$k_2 = 3.04 \times 10^7 \exp(-\frac{\Delta H}{RT})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MDEA</td>
<td>Batch mode w.r.t.</td>
<td>T:25; A:0–1 G:0.015–0.03 m³/hr</td>
<td>99, NA</td>
<td></td>
<td></td>
<td>It doesn’t polymerize unlike primary &amp; secondary amines</td>
<td>[166]</td>
</tr>
<tr>
<td></td>
<td>AMP</td>
<td>Double stirred cell absorber (BS)</td>
<td>T:47 (flue gas);</td>
<td>90, NA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>Double stirred cell absorber (BS)</td>
<td>T:25–50; P:0.1; A:0.5–1.2</td>
<td></td>
<td>99.11 at 60 °C, NA</td>
<td></td>
<td></td>
<td>Density and viscosity increases with concentration &amp; decreases with temperature.</td>
<td>[168] [180]–[107]</td>
</tr>
<tr>
<td></td>
<td>DEAB</td>
<td>Packed laminar jet absorber (lab scale)</td>
<td>T:25 A:1–2</td>
<td>&gt; 95, NA</td>
<td></td>
<td>k_{DEAB} = 4.01 \times 10^{13} \exp(-\frac{\Delta H}{RT})</td>
<td>Mass transfer depends on column height &amp; absorbent type.</td>
<td>[169] [54]</td>
</tr>
<tr>
<td>Mixed Solvents</td>
<td>MEA blends</td>
<td>Packed (CC; pilot)</td>
<td>T:25–50 A:3–5 G:100</td>
<td>~100, 0–0.59</td>
<td></td>
<td>$K_C_{CO_2} = K_{CO_2} \exp(\Delta H_{CO_2}^{enthalpy}/RT) \exp(\Delta G_{CO_2}^{enthalpy}/RT)$</td>
<td>Blend has better energy efficiency</td>
<td>[170]</td>
</tr>
<tr>
<td></td>
<td>(A₁–A₂)</td>
<td>L:2.5–5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass transfer increases with liquid loading.</td>
<td>[171]</td>
</tr>
<tr>
<td></td>
<td>MEA-NaOH</td>
<td>Packed (CC; pilot)</td>
<td>A₁:1.2, A₂: 3 1:3.8–29.3 C:2 L₂: 3.8–22.9 T:25; T:25–50</td>
<td>NA, 0–0.5</td>
<td></td>
<td></td>
<td>Structured packing performs better</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BDA-DEEA</td>
<td>Packed (CC, BS)</td>
<td>T:40 (absorption); T:90 (desorption) G: 24.78</td>
<td>96 (HCL), 48 (HCC), 11 (HCE) than MEA with 5 M</td>
<td></td>
<td>Carbamate &amp; Bicarbamate formations: $BDACOO^+ + CO_2 \rightarrow BDACOO^+ CO_3Na$</td>
<td>Theoretical study validated with NMR studies.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEA-K₂CO₃</td>
<td>Split flow (CC, bench scale)</td>
<td>T:115 L:63.66 m³/h</td>
<td>99, NA</td>
<td></td>
<td>BDA + CO₂ + H₂O → BDACOO⁻ + CO_2^0 + H⁺ + BDACOO⁻ + CO_2 + H₂O → BDA(CO₂)⁻ + H₂O⁺</td>
<td>Amine provides an efficient way of CO₂ capture.</td>
<td>[173]</td>
</tr>
<tr>
<td></td>
<td>AMP-PZ</td>
<td>Packed (pilot)</td>
<td>L/G:2.9; packing height ~10 m</td>
<td>90, NA</td>
<td></td>
<td>$q_{hmin} = \frac{C_{HMIN}^1}{\Delta H_{CO_2}}$</td>
<td>Regeneration energy is 3700 kJ/kg CO₂.</td>
<td>[77]–[84]</td>
</tr>
<tr>
<td></td>
<td>PEI-SiO₂</td>
<td>Packed (bech scale)</td>
<td>L/G:33.66 m³/h</td>
<td>N/A</td>
<td></td>
<td>A high absorption efficiency, a high desorption efficiency, and a low regeneration energy penalty</td>
<td></td>
<td>[120,121]</td>
</tr>
</tbody>
</table>
successful in achieving 20% reduction in regeneration energy and 45% in the absorbent circulation rate apart from showing a significant improvement in thermal and oxidative degradation resistances [67,77–83]. It has been recently reported by Dash et al., [84] in their simulation studies that 90% CO2 capture could be achieved employing 22 wt% AMP+8 wt% PZ. Aqueous ammonia has been employed as a solvent due to its high CC efficiency, high absorption capacity, low regeneration costs, easy availability, ability to remove SO2, NOx along with CO2 simultaneously and the value added salts that could be used as fertilizers [43,85–90]. Due to their distinct advantages, the technology has been upgraded to pilot scale [91,92]. Aqueous potassium carbonate has also been reported as an absorbent for CC due to its low enthalpy requirements, low cost, less toxicity and high degradation resistance. To offset its very low mass transfer rate, promoters like inorganic salts of arsenites, vanadates, borates and silicates; organics like amines and their derivatives, alkaline amino acids like arginine and biological enzymes like carbonic anhydrase have been reported [93–102]. Potassium carbonate supported on MgO is reported to achieve an efficiency of 99.4% CO2 [103]. Studies have also been conducted on tray absorption tower for CO2 capture with > 95% CO2 capture efficiency by Mores et al., [104].

In the recent past, imidazolium ion based ionic liquids (ILs) have been employed for their unique properties viz, non-inflammability and non-explosivity, high thermal and chemical stabilities, almost negligible vapor pressure, tunable physico-chemical properties, higher reaction velocity and selectivity. They are also economical, efficient and are compatible with membrane technology due to their non-wettability [105–107]. They are also blended with amines to derive the advantages of both systems [108–113]. Besides ILs, binding organic liquids (BOLs) which too exhibit tunable physico-chemical properties are being employed as they are highly energy efficient during the solvent regeneration [114–119]. Alcohol/amine/water blends and poly-ethylenimine (PEI) immobilized on silica (SiO2) support have been recently reported as novel absorbents for CC [120,121].

2.1.2. Contactors for Absorption

From operation angle, the precooled power plant flue gases enter the absorption system at near atmospheric pressure. The CO2 lean absorbent from the stripper is pumped into the absorber in a countercurrent fashion. CO2 is absorbed to form carbonate or bicarbonate and other compounds. Since, it is an exothermic reaction, interstage cooling in contact towers is desirable for maintaining high absorption efficiency. The CO2 rich absorbent exiting the bottom of the absorber is pumped to the top of the stripper operating at 100–150 °C under the influence of a thermal swing operation. The reboiler at the bottom generates stripping steam which meets CO2 rich absorbent as it flows down the stripper. The temperature swing reverses the CO2 absorption reaction and returns the same to the gas phase. The CO2 thus released from the stripper is compressed and sent for storage [9]. Extensive literature has been reported in the development of efficient gas–liquid contactor configurations, solvent systems and stripper configurations. The main focus of energy investigations is to achieve high capture efficiency with minimal energy penalty [122,123].

Various absorber configurations are employed for CO2 absorption viz., packed bed, bubble column, rotating packed bed and tray towers. Cousins et al., [124] has dealt with process flow sheet modifications for CO2 absorption to make it more energy efficient by employing multiple columns in the pre-treatment stage, inter-stage temperature control to achieve the desired temperatures of 40–60 °C for optimal CO2 absorption, heat integrated stripping to reduce the energy requirement (by half or one third) in the regeneration process and use of the split flow process to achieve energy requirements by 50%. Other retrofit options attempted are vapor recompression in the stripping section, matrix stripping in which number of strippers operate at different pressures in a matrix pattern and use of the overall heat integration [69,125–133]. The major factors that affect the CO2 absorption CC by absorption in a packed column are physical properties of the solvent, liquid and gas flow rates, CO2 partial pressure/total pressure of the system, temperature, absorbent concentration, nature of packing and CO2 loading on the solvent [134]. Among the physical properties, the surface tension of the solvent has influence on mass transfer and increased effective packing area [135]. The CO2 partial pressure has a direct influence on the CC efficiency due to the increase in the driving force for the mass transfer [136–138]. Regarding the effect of gas flow rate, clarity is still required [135,138–140]. The liquid flow rate has been found to have a positive impact on the CO2 capture efficiency [135,141,142]. The absorbent concentration has a direct influence on CO2 capture efficiency, heat of reaction, temperature and the CO2 vapor pressure [135,138,143]. A high absorption temperature leads to increase in viscosity, CO2 vapor pressure and decrease in the solubility of CO2 [139]. In a packed column, the nature of packing viz., structured or random has a vital role in the capture efficiency. The former provides much superior performance due to higher geometric surface area per unit volume. Apart from the nature of packing material, other factors like packing arrangement, corrugation angle, crimp height can influence the absorbed performance [144,145]. Absorption studies have also been reported employing rotating packed reactor (RPB) using P2 and a blend of P2 and DETA for 10% CO2 with N2. RPB is found to be better than PB in terms of enhanced gas–liquid contact area and mass transfer rate and a smaller size for achieving the same capture efficiency [146]. Gas flow rate and scavenger contents are the most critical parameters influencing the CC and dissolved oxygen [147]. Bubble column reactors have been reported for CC using ammonia as a solvent. The contactor geometry (liquid column height to diameter ratio) along with ammonia concentration and temperature have positive influence on the performance while inlet CO2 concentration and the flue gas rate had negative influence on the capture efficiency [148]. Recently mini-channel reactor which offers high surface area to volume ratio has been employed for the absorption of CO2, from its mixture with N2 using DEA to achieve 100% absorption efficiency with 4 times increase in mass transfer coefficient and high specific interfacial area [149].

2.1.3. Modeling and kinetic studies

Two main approaches are adopted for modeling CO2 absorption viz., equilibrium stage and rate modeling concepts. The latter is more extensively employed. Khan et al., [150] validated a rate based model employing fast second order kinetics for the CO2–MEA system in a packed column considering the enthalpy changes in both gas and liquid phases. Guo and Zhang [151] and Dash et al., [84] employed rate fraction in Aspen Plus for ammonia and AMP-PZ blended absorbents. Chikukuwa et al., [152] reviewed the models employed for CO2 absorption and stripping using MEA as solvent. Flue gas composition and flow rate, reboiler duty, CO2 capture level and L/G ratio have been used for evaluating the dynamic behavior. Models based on two film theory have been found to be more successful in predicting absorber performance as compared to penetration theory. Software platforms like gPROMS, Aspen Plus, Aspen HYSYS, ProMax, Aspen Customer Modeler, Tsweet, Aspen Plus Dynamics, MATLAB with ODE solver and Simulink have been employed for the modeling studies [153]. CFD based models have been employed to understand the hydrodynamic phenomenon in absorbers. Sarkar et al., [154] studied the fluidized bed regenerator design employing a multiphase CFD modeling using solid absorbents under plug flow and well mixed flow conditions. Sub-grid filtered CFD models have been reported for simulating flow in larger absorbers besides incorporating desorption kinetics [155,156]. Recently physical absorption by the rectisol process was
comprehensively reviewed by Gatti et al., [157] with respect to various process configurations, simulation of staged regeneration and auto-refrigeration via mechanical vapor recompression using Aspen plus software platform.

Kinetic studies have been conducted by Shen et al., [158] for absorption of CO2 with aqueous K2CO3 promoted by arginine in wetted wall column at various temperatures. The kinetics was found to follow pseudofirst order regime with rate constants of 33,641 L/mol s and 85,367 L/mol s at 313 and 325 K respectively with activation energy of 71.9 kJ/mol. The reaction was reported to follow zwitterion mechanism. Larachi et al., [159] employed emulsions of amines (DEA) with ionic liquids for CO2 absorption in a stirred cell contactor to understand the influence of various parameters like amine concentration, temperature, CO2 partial pressure, agitation speed on CO2 absorption among which agitation speed was found to have the most vivid impact. The techno economic and scale up aspects of the post-combustion CC processes were reviewed by Saiprasad and Raghavan [160]. Table 2 gives the summary of Technological options for CC in terms of contactor, absorbents employed, CC efficiencies achieved along with relevant kinetic models.

From the above section on absorption, we understand its critical role in CC and various developments of the technology has witnessed in terms of development of novel absorbents, like IIs, BOLs, amine blends, etc. and novel contactors like RPB, mini-channel reactors for achieving process intensification besides developing rigorous hydrodynamic and kinetic models to explain the process effectively. The challenges posed by this technology are the development of novel green cost-effective solvents to reduce the regeneration costs and design of efficient contactors with energy integration and process intensification employed.

2.2. Gas-sold adsorption

Adsorption facilitated CC processes are promoted by gas-solid intermolecular forces. The kinetic diameter of molecules present in flue gases varies between 2.65 and 3.75 Å with kinetic diameter of CO2 being 33 Å. Wide differences exist in their electronic inue gases varies between 2.65 and 3.75 Å with kinetic diameter of CO2 being 33 Å. Wide differences exist in their electronic

2.2.1. Pressure, thermal and electrothermal swings

2.2.1.1. Pressure and vacuum swing adsorption (PSA). It was introduced in early seventies by Turnock et al., [174]. Kao et al., [175] employed PSA for significant improvement in the selectivity of a membrane possess for separations of a helium–methane mixture. Dabrowski et al., [176] reviewed theoretical and experimental applications of adsorption technology. PSA technology is conventionally performed at higher pressures in feed (adsorption) and atmospheric pressure in regeneration in PSA or less than atmospheric pressure in VSA. Its operation is periodic (swings) in nature. It is used for removal of bulk contaminants at comparable higher concentrations. Simulation studies employing a two stage V-PSA (Vacuum PSA) process with Zeolite 5A as adsorbent have been recently reported by Zhen Liu et al., [177] to achieve a CO2 purity of 96% in a two bed and 70% purity for single bed process for 15% CO2–85%N2 mixture. Lopes et al., [178] and Grande [159] have reported on a 10 steps PSA units with activated carbon adsorbent as well as engineering approaches of PSA performance. Vacuum swing adsorption has also been reported employing multilayered adsorption system of 13X zeolite and activated alumina, F200 and silica based Sorbead as protective pre-layers. Langmuir extended BET and multi-molecular sorption equations for the simulation studies to achieve 91% CO2 purity [179]. VSA has also been employed to study the performance of the adsorbent of UiO66 (metal organic framework) for the capture of CO2 from dry and wet flue gas containing 15% CO2. Around 70% capture efficiency could be achieved up to 50 cycles with a six step VSA cycle. Water vapor in the flue gas has a negative influence on the CC [180]. Hedin et al., reviewed the use of various micro- and mesoporous physical sorbents and amine modified mesoporous silica using temperature or vacuum swing adsorption and stressed the need for more effective adsorbents and the energy integration in power plants for better thermodynamic efficiency [181]. Danga et al., [182] employed the Dual Piston pressure swing adsorption (DP-PSA) system for the characterization of novel adsorbents for Zelite 13X and isothermal model for cycle times greater than 10 s with pressure ratios of 2–3. Gas flow pattern studies on the multistep PSA process have been performed by Nathalie Casas et al., [183,184]. Recently Su et al. [185] reported the use of dual column temperature/vacuum swing adsorption using amine loaded carbon nanotubes as adsorbents to achieve 67% CO2 concentrations.

2.2.1.2. Temperature swing adsorption (TSA). The TSA is carried out at moderate temperatures of around 40 °C and desorption occurs at around 120 °C. It is used for the removal of contaminants at low concentrations. Both TSA and PSA were commercialized in the early sixties and were subsequently improved with novel, effective, stable and recyclable adsorbents. While the conventional adsorbents used for TSA and PSA were silica gel, activated alumina, metal oxides and zeolites, the novel ones are metal organic frameworks, activated carbon, graphite and porous polymers such as honeycomb monolith [186]. The major drawbacks of TSA over PSA are longer desorption times, higher energy requirements and rapid adsorbent deactivation due to coking at high temperatures [187]. Pilot scale tests (1 kW) have been reported using carbon and amine based adsorbents in a fluidized bed contactor with TSA as the regeneration strategy [188]. Veselovskaya et al., [189] employed a composite K2CO3/Al2O3 adsorbent to capture CO2 from air using TSA for regeneration. It has been observed that with an increase in regeneration temperatures from 150–200 °C to 250–300 °C increases CO2 capture is increased upto 5 wt% and that the composite materials exhibited high stability up to 80 cycles. Hedin et al., [181] identified adsorbents suitable for rapid TSA viz., mesoporous materials like zeolites, carbon molecular sieves, metal organic frameworks; other microporous physi-sorbents like MCM41, silica and amine modified mesoporous silica.

2.2.1.3. Electrothermal swing adsorption (ESA). It employs Joule effect by passing electricity through a packed column [190]. Grande et al., [190,191] employed activated carbon honeycomb monolith as an adsorbent separation of CO2 in low concentrations in the flue gas streams. The desorption is not through resistive
heating of the matrix, but through a direct electrical effect contribution sorbate–sorbent interactions [187,192]. The adsorbent to be employed in this process has to be conducting to promote electrical swing [187]. ESA is more economical than TSA and PSA with suitable adsorbents like activated carbon fiber materials are employed. More lab and pilot studies have to be done on ESA before its commercialization [193].

Pevida et al., [194] examined various regeneration strategies employing TSA, VSA and VTSAs employing activated carbon as an adsorbent to capture CO2 from CO2–N2 mixture. They found that for single bed cycle configurations, the productivity and CO2 recovery followed the order viz., TSA < VSA < VTSAs for achieving a maximum CO2 recovery of 97%.

2.2.2. Adsorbents and their selection

An ideal adsorbent should have high CO2 capture capacity, easy regenerability, stability, large pore dimensions and recyclability. Carbon fiber monoliths (poly acrylo nitrile (PAN) and Viscose Rayon) and activated carbons are reported for ESA and PSA [192,193,195]. Table 2 highlights the efficiencies of various adsorption for CO2 capture. High temperature adsorbents like calcium chabazite, 13X zeolites and K2CO3 based HTC zeolite, hydrotalcite-like (clay minerals) compounds containing nickel and iron cations with and without boehmite alumina have been employed as adsorbents. Their adsorption capacity is found to be 2.5 mmol/g and exhibited high thermal stability and activity over a wide range of temperatures [196]. Pilot test results have been reported by Sjostrom et al., [188] for hundred adsorbents in a fixed bed contactor. Amine and carbon based adsorbents were tried the former exhibited high adsorption capacity whereas the latter has shown the higher cyclic stability though with low CC capacity [186]. Zeolite 5A and multilayered zeolite 13X with pre-layers of F200 and silica based Sorbad W5 have been employed for adsorption of CO2 from a mixture of CO2–N2 using VPSA regeneration in a multi-bed column [177,179]. Nanoporous materials (1–100 nm) like zeolites, activated carbon, nano-hollow structured material (1–10 nm) like carbon nanotubes, CaO nanopods and nanocrystalline particles like lithium silicate, Li2ZrO3 have been reported. Future research efforts need to be directed towards the development of novel and cost effective synthesis protocols followed by scale-up [122]. Recently, amine modified TiO2 nanotubes, TEPA modified metal organic frameworks (Mg–MOF-74) have exhibited the highest adsorption capacity of 167.64 mg/g with good cyclic stability [185,197,198]. Recently polyethyleneimine (PEI) incorpo- rated metal-organic framework (MOF) adsorbents were able to achieve selectivity of CO2 over N2 up to 770 at 25°C since the available active sites would maximum (52 mm/g at 15%) since the available active sites would become a limiting factor beyond certain concentration of the adsorbate molecules. Adsorption capacity decreases with tempera- C)

ture, feed rate and the amount of the adsorbent used. Auta et al., [209] observed an optimal CO2 at which adsorption capacity is maximum (52 mm/g at 15%) since the available active sites would become a limiting factor beyond certain concentration of the adsorbate molecules. Adsorption capacity decreases with tempera- C)

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To summarize the developments, the microporous and meso- porous solid adsorbents have the highest potential for large scale CO2 capture. The SiO2/Al2O3 ratio and incorporation of cations in their structure can enhance their adsorption capacity. The impregnation of polyethyleneimine into MCM–41 is reported to enhance CO2 adsorption 24 times. The selectivity and adsorption capacity achieved so far are not attractive enough for large scale post combustion CO2 capture. Metal organic frameworks (MOF), which are endowed with carefully sized cavities, have high CO2 capture potential, low energy consumption for desorption and higher impurity tolerance. On a comparative basis, the active area per unit weight of MOFs is around 1500–4500 (m2/gm) as compared to 400–1000 (m2/gm) for activated carbon and 1500 m2/gm for zeolites. Supporting liquid absorbents on porous solid substrates is gaining momentum, the focus is on minimizing thermal instabil- ities, fouling tendencies and SO2 induced degradations.

2.2.3. Contactors for adsorption

Fixed bed (single or multiple columns), normal, bubbling and ultra-sound assisted fluidized beds and moving bed contactors are used for adsorption due to their relatively simple operation and design. The critical parameters that affect the functioning of the fixed bed contactors are CO2 concentration in the feed, tempera- C)

ture, feed flow rate and the amount of the adsorbent used. Auta et al., [209] observed an optimal CO2 at which adsorption capacity is maximum (52 mm/g at 15%) since the available active sites would become a limiting factor beyond certain concentration of the adsorbate molecules. Adsorption capacity decreases with tempera- C)

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inter-stage heat integration for improved energy efficacy using sorbents like K$_2$CO$_3$, Na$_2$CO$_3$ modified MgO and Li$_2$SiO$_4$. Each stage contains an absorber, a regenerator and heat exchanger for intra-stage heat recovery. Between adjacent stages, an absorber at high temperature is thermally integrated with a regenerator at lower temperatures for necessary thermal balance. It is estimated that for a three stage process, a net electrical efficiency of 32.8% was achieved in power plant of 500 MW capacity.

Table 3: Summary of adsorption based carbon capture.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Reactive separator</th>
<th>Operating conditions P,T,C,G</th>
<th>CO$_2$ capture (%)</th>
<th>Kinetics/mass transfer</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>rayon – HCM</td>
<td>PBR(TSA)</td>
<td>$S_a$: 1873.9; AT:950; CT:650; FRR:0.5</td>
<td>97, 0.2</td>
<td>$\frac{q}{q_{\infty}} = \frac{q_{\infty}}{q_i} + \frac{t}{k_f}$</td>
<td>Ad-C is twice that of conventional activated carbon &amp; 1.5 times ZiF.</td>
<td>[232] [243]</td>
</tr>
<tr>
<td>Activated carbon-HCM</td>
<td>PBR(ESA,8&amp;6-cycle, LS)</td>
<td>$T$:24; P:0.1; ICC:4.51; 4-step cycle: 99.6, NA &amp; 21.7% (purity)</td>
<td>multi-site Langmuir model, enthalpy ~ 25kJ/mole</td>
<td></td>
<td>Decrease in electrical efficiency with thermal load.</td>
<td>[236]</td>
</tr>
<tr>
<td>Fly ash + PEI + PEG</td>
<td>PBR(TSA,LS)</td>
<td>$T$:70; P:0.11; $S_a$: 24 h</td>
<td>6-step cycle : 81.4, NA &amp; 66.6% (purity)</td>
<td></td>
<td>Energy saving &gt; 5 times in fitep cycle</td>
<td>[244]</td>
</tr>
<tr>
<td>XZ &amp; K$_2$CO$_3$ promoted HTC</td>
<td>PBR(VPSA,LA)</td>
<td>$T$:120–250; P:0.003; 8x12 mesh</td>
<td>95, NA &amp; 97.2% (purity)</td>
<td>$\frac{C}{C_0} = \frac{C}{C_0} + \frac{t}{\tau}$</td>
<td>Operational Simplicity of reactor, reduced cycle time and Small bed sizing factor.</td>
<td>[246] [247]</td>
</tr>
<tr>
<td>ZK + MEA, ZK + IPA</td>
<td>PBR(PSA,LS)</td>
<td>P:0.1; T:77.5; ICC:15; $S_a$:14.9; $c$:0.044</td>
<td>NA, 0.01611(5Z); NA, 0.01998(MEA); NA, 0.02272(IPA)</td>
<td>2$RNH_2 + CO_2 \rightarrow RHCOO^{-} + RH^+ + CO_2$</td>
<td>Hybrid absorption-adsorption</td>
<td>[248] [249]</td>
</tr>
<tr>
<td>NPC10</td>
<td>PBR(TSA, LS)</td>
<td>$S_a$:1314(MS); $S_a$:1327 (STS)</td>
<td>NA, 0.041</td>
<td>NA, 0.0288(MS)-CO$_2$</td>
<td>Selectivity over N$_2$ is &gt; 25:1</td>
<td>[250]</td>
</tr>
<tr>
<td>Co-MOF-74 (MS)</td>
<td>PBR(PSA, LS)</td>
<td>$S_a$:900; $D_p$:0.5</td>
<td>NA, 0.406(MS)-H$_2$O</td>
<td>NA, 0.0605(STS)-H$_2$O</td>
<td></td>
<td>[251]</td>
</tr>
<tr>
<td>Co-MOF-74 (STS)</td>
<td>PBR(VPSA, LS)</td>
<td>T$<em>{m}$:1; T$</em>{st}$:12</td>
<td>60–70%NA, 60% (purity)</td>
<td>throughput (TPD) $\times \frac{En_{	ext{production}}}{\text{cycpe}} \times \text{specific productivity} = k_{WC} \frac{\text{mole}}{\text{c}}$</td>
<td>25% capacity decrease due to water vapor after 50 cycles.</td>
<td>[253] [246]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>PBR(1bed,3step, VSA, LS)</td>
<td>T: 60; $lp$:0.113; $P_{Vp}$:3; $T_{in}$:3; $S_a$:900; $D_p$:0.5</td>
<td>69.5, NA</td>
<td>Dual-site Langmuir equation has been adopted</td>
<td>Increased energy penalty and variation in hydrophobic nature of activated carbon due to water presence.</td>
<td>[253]</td>
</tr>
<tr>
<td>ZK-APG, 5A zeolite</td>
<td>PBR(3bed,8-step, VPSA, LS)</td>
<td>T:35; P: 0.007–0.008</td>
<td>85–95, NA, 73–82% CO$_2$ purity</td>
<td>Langmuir adsorption isotherm adopted isotherm for CO$_2$</td>
<td>Increased higher cost with an energy consumption of 1.79–2.14MJ/kg of CO$_2$</td>
<td>[255]</td>
</tr>
<tr>
<td>BZK, NaX, KX &amp; CaX</td>
<td>PBR(PSA, LS)</td>
<td>$L_0$=0.05, $P_{0}$=0.05–0.75, $S_a$:931; $x$</td>
<td>NA, 0.219,12</td>
<td>Adsorption kinetics model has been investigated by the Zero-Length Column technique (ZLC)</td>
<td></td>
<td>[256]</td>
</tr>
<tr>
<td>ZK</td>
<td>MBA(P/SA, LS)</td>
<td>80, NA, 97% purity</td>
<td>Extended Langmuir Isom thr was used</td>
<td>54.4% of energy regenerated from Adsorber.</td>
<td></td>
<td>[258]</td>
</tr>
<tr>
<td>FAC</td>
<td>SAFR(LS)</td>
<td>90, NA</td>
<td>Langmuir Isom thr is adopted, Increase of temperature is very small (2–3 K).</td>
<td></td>
<td></td>
<td>[259] [260]</td>
</tr>
<tr>
<td>Amine – silica aerogels</td>
<td>PBR(LS)</td>
<td>Silane: silica ratio $= 2:1$ T:95°C</td>
<td>2.61 mmol/g with 100% CO$_2$ at 1 bar and 25°C, NA</td>
<td>N$_2$ adsorption isotherm</td>
<td>Adsorption capacity of 1.76 mmol/g</td>
<td>[251]</td>
</tr>
<tr>
<td>TiFA-Mg-MOF-74</td>
<td>PBR(LS)</td>
<td>Regeneration temp is 250–300°C</td>
<td>4–4.9 wt%, 8.31 mmol CO$_2$/g absorbent, NA</td>
<td>N$_2$ adsorption-desorption isotherm</td>
<td>Increase in Desorption temperatures</td>
<td>[189] [197,</td>
</tr>
</tbody>
</table>
2.2.4. Kinetic and modeling studies

Employ pseudofirst and second order kinetics, intra-particle diffusion models have been employed to simulate the adsorption process. Yusup et al., [222] found that pseudo-second order model fitted the data best and the activation energy for the physisorption process was found to be less than 42 kJ/mol. Erto et al., [223] have investigated the kinetic, thermodynamic and regenerative studies on adsorption using synthetic activated carbon (PS5 from coal tar pitch). They also found that the adsorption process is reversible in nature with optimal desorption temperature at 100˚C being the controlling parameter. The adsorption rate was found to increase with inlet CO$_2$ concentration and temperature. The sorbent was found to be stable even after the 15 adsorption–desorption cycles. CFD modeling was employed to study the hydrodynamics and adsorption process. Ryan al. [224] have tried various multi-phase models and found that Eulerian–Lagrangian model (FLUENT) has successfully simulated the fluidized bed reactor performance with silica-supported amine sorbent. Daud et al., [225] have various mathematical models to explain the complex phenomena associated with CC in a fixed bed reactors. The adsorption equilibrium relationship can be explained by Langmuir–Freundlich, Ideal adsorbed solution theory (IAST), extended Langmuir–Freundlich, O’Brien–Myers, multisite Langmuir, Virial, Toth and dual site Langmuir isotherms mostly assuming plug or axial dispersed flow [226–242].

Table 3 summarizes the engineering aspects of the adsorption process in terms of nature of adsorbents, contactors, mode of operation, operating and critical parameters besides kinetic aspects.

Like absorption, adsorption is also a very established technology for gas–solid operations. It has been successfully employed for both pre- and post-combustion carbon capture and significant improvements have been done in the identification of novel and cost-effective adsorbents like nano-materials, biomass materials and those from industrial wastes. To reduce the cost involved in regeneration, a combination of vacuum and thermal swing adsorption cycles showed great potential. Many models have been identified to explain the adsorption–desorption processes among which modified Langmuir isotherm was the most popular. The contactors being employed for adsorption based CC witnessed great improvements like multistage-fluidized bed with energy integration to reduce energy consumption significantly.

2.3. Membrane technology

2.3.1. Membrane separation and membrane materials

The absorption adsorption processes for CC require contacting towers of large diameter (18–20 m) and length (25–30 m). Membranes with as much as 1000 times more surface area per unit volume are much more effective in minimizing the size of contact towers. An effective membrane system for CC has to be endowed with high adsorption capacity without CO$_2$ penetration into the bulk, high reversibility, highly selective to CO$_2$ with insignificant sorption capacity to N$_2$, CH$_4$, H$_2$ and others in flue gas, high resistance to flue gas poisoning by Sox, NO$_x$ and H$_2$S, ease of fabrication, high stability at elevated temperatures and ability to perform efficiently at lower thicknesses.

Membrane technologies can be utilized both for pre-combustion and post-combustion CC. In case of the latter, membrane contactor has been successfully employed for gas–liquid absorption while they can be used for separation of CO$_2$ from the flue gases employing a wide variety of membrane materials. Membrane separation is developing into a process intensification tool for reactive absorption processes. Ceramic membrane contactors are employed in cases where significant absorption could not be achieved with conventional absorbers.

CO$_2$ permeation increases when there is a chemical affinity with specific molecular groups present in the membrane. Several CO$_2$ selective membranes have been reported for CC from flue gases. The Department of Energy, USA reviewed the membrane development for CC, their stability, performance, interrelationship of their properties and mechanisms applicable in different CO$_2$ selective separation processes [261]. Cost savings up to 35% have been reported to be achieved in a coal fired power plant operated under vacuum conditions [262–264]. Membranes provide semi-permeable barriers that separate substances by accordingly, three general transport mechanisms viz., Knudsen-diffusion, solution–diffusion, adsorption–diffusion, molecular sieving and ionic transport mechanisms. They are available in various forms viz., organic (polymeric) or inorganic (carbon, zeolite, ceramic or metallic) in porous to nonporous forms. Membranes act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate [43]. They offer various advantages like viz., no flooding at high flow rates, no unloading at low flow rates [265], high surface area per unit contact volume, independent control of gas and liquid flow rates, compactness and scalability. The advantages outweigh their fouling problem [266]. From operational point of view they offer low maintenance cost with no moving parts, relatively low capital cost and small physical footprint which makes it favorable for platform and less energy intensive operations.

Cahn and Li [267] reviewed the liquid membrane process for the separation of hexane from heptane. Ward III et al., [268] reported silicone/poly carbonate membranes for on-board generation of nitrogen enriched air used as an inert gas. Karos and Flemming [269] reviewed on material selection, membrane synthesis, and modular concepts in their scale-up and system characteristics. Armor [270] highlighted the utility of catalytic inorganic membrane reactors for refinery products. Corti et al., [271] developed a methodology for the CO$_2$ separation from membrane reformed synthesis gas. Membrane based pre-combustion process of integrated gasification combined cycle has been critically analyzed by Colin a Scholes [272]. The major material development challenges in membrane processes would be membrane porosity and thickness, non-wetting characteristics, hydrophobicity, non-polar nature and pore size distribution. The critical parameters are flue gas composition, temperature and flow rate, high parametric sensitivity, selectivity to be achieved, need of high quality energy, etc. [273].

2.3.1.1. Microporous membranes. Generally inorganic membranes and facilitated transport membranes fall under this category [261].

The working principle of microporous membranes is indicated in Fig. 4. The membrane support has an asymmetric porous structure (except palladium-based membranes) to minimize flow resistance [274]. They can be configured as modules of hollow-fibres or flat plates. The different types of membranes employed CO$_2$ capture are given in Fig. 5. Hollow-fiber polypropylene membrane contactors are reported to give 97% capture efficiency with standard 3M MEA solutions [275]. The flat sheet membrane contactor was found to be better than that of hollow fiber.
membrane contactors provide better CO₂ absorption flux as compared to hollow fiber membrane contactors [276]. Various membrane materials have been employed for above configurations viz., PVDF (polyvinylidene fluoride), PP (polypropylene), PTFE (polytetrafluoroethylene), PEI (polyetherimide), PSf ( polysulfone) and PMP (polymethylpentene) Teflon-AF [277]. Among these, PP is economical but has low chemical resistance but PVDF and PTFE though chemically resistant are more expensive. Hence, the need is to develop novel cost effective membrane materials and solvent systems that facilitate good CO₂ capture at low cost. Gas absorption occurs in the gas filled membrane pores. The membrane support plays a key role in enhancing the system performance with marginal influence on selectivity. Hyper-cross-linked networks consisting of aromatic rings connected to polymeric matrices have been reported to form porous networks. Modification of the network surface could be achieved through functionalization of hyper-cross-linked layers [278]. Porous inorganic membranes are high temperature CC processes. The mechanisms of CO₂ separation in inorganic membranes are based on adsorption selectivity and surface diffusion with relatively low separation factors. Microporous silica membranes containing amine functional groups have been reported for CO₂ separation from flue gases [279]. The CO₂ capture can also be achieved with molecular sieve membranes in which CO₂ separation occurs on account of size discrimination within the channels of its porous structure.

2.3.1.2. Dense membranes. CO₂ permeation involves selective passage of gas molecules through a dense membrane (generally polymeric). Its permeability and selectivity would be critical parameters in the process optimization. Their working principle is given in Fig. 6. A solution–diffusion or a molecular sieving mechanism explains the process. Knudsen-diffusion mechanism has also been reported to conform to this system. Dense polymeric membranes are successfully used in CC due to their high permeability and flux achieved [280]. Various materials viz., Te_N, ceramic, ceramic composite, PDMS (polydimethy siloxane), DMS (dimethylsiloxane), PSf, Pebax, silica–alumina, polyfluoroaniline– fluoroaniline copolymer, zeolite Y, polyamide-imide, PES, PPO (polypropylene oxide), PVAm (polyvinylamine), CNT (carbon nanotube), POX (polyaryloxyphosphazene)-PDMS crosslinked, TM (tetramethyl)-PSf, HF-PSf, imidazolium, LDPE (low density polyethylene), PEEK (polyether ether ketone), PBI (polybenzimidazole), polyurethane, carbon molecular sieves, etc. are employed [278]. Wang et al., [281] achieved high CC with selectivities of above 100 and permeability of 743 Barrer (1 Barrer = 7.5 x 10⁻¹⁰ cm³ (STP) cm/cm² s kPa) at 10 bar employing hybrid membrane made of Pebax-PEG-MWCNT (multiwalled carbon nano-tube). Mixed matrix membranes of polyvinylalcohol containing amines with MWCNTs dispersed as mechanical reinforcing fillers demonstrated high stability for gas separation at high pressures up to 1.5 MPa. Selectivities and permeabilities of 43 and 836 Barrers have been achieved even at such high pressures [282]. Marono et al.,[283] developed a novel hybrid membrane system based on potassium carbonate doped hydrotalcite-catalyst, for pre-combustion CC and H₂ production.

2.3.1.3. Supported liquid membranes (SLM). In this system, the liquid is dispersed on a porous or non-porous support. The CO₂ in the flue gas is physically or chemically absorbed into the liquid and passes through the membrane support. Viscosity of the liquid is found to play a key role in the system design and the performance. The SLM working is demonstrated in Fig. 7 below. Typical examples are TEG liquid membranes modified by Na-Y nano-zeolites, SLm with fluoroalkyl-functionalized RTILs, DEA supported on polyvinyl alcohol, ionic liquids [mim][Te_N], [emim][CF₃SO₃], [mim][PF₆], [H₃NC,H₄mim][Te_N], enzyme of carbonic anhydrase, etc. supported on polymer, all ionic liquids to be put together. Ionic liquids of [emim][BF₄], [bmm][BF₄], [hmim][BF₄], [bmm][PF₆], [hmim][Te₃N], [bmm][Te₃N] supported on polymer or PVDF, [bmm][N(CN₂)], [emim][B(CN₂)], etc. supported on PES, etc. [242]. Ionic liquids are used to eliminate...
the solvent evaporation step and as to achieve higher stability (2012) [122]. Selection of the support was found to have marginal influence on the selectivity but it was found to be crucial in determining the stability of the system. SLM is an upcoming technology yet to be commercialized at an industrial scale though promising results have been reported at lab scale [273,284,285]. Fig. 7 shows the variety of membrane materials employed for CC.

2.3.2. Membrane contactors and modeling studies

Packed columns have been the most commonly employed contactors for membrane based CC. The critical design parameters for scale-up are pressure drop, temperature and water condensation effects, flow rates and dispersion effects of gas mixture and solvents and mechanical stability. An average volumetric CO₂ absorption capacity of 1 mol/m³ s can be taken as a baseline (2012) [122]. Selection of the support was found to have marginal effects on the selectivity but it was found to be crucial in determining the stability of the system. SLM is an upcoming technology yet to be commercialized at an industrial scale though promising results have been reported at lab scale [273,284,285]. Fig. 7 shows the variety of membrane materials employed for CC.

### Table 4
Summary of cryogenic based carbon capture.

<table>
<thead>
<tr>
<th>Process</th>
<th>Membrane/Reactive separator</th>
<th>Operating parameters</th>
<th>Kinetics/mass transfer</th>
<th>Challenges</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDC</td>
<td>Micro-porous Membranes</td>
<td>PT, Pore size and ε of the membrane-membrane wettabillity</td>
<td>Reaction kinetics depends on solvent.</td>
<td>Wetting of the membrane</td>
<td>Membrane-solvent combination &amp; wetting are critical at high reaction rates.</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Hollow fiber and Flat Sheet</td>
<td>Liquid flow area</td>
<td>- Pore diffusion depends on membrane support.</td>
<td>- Limited long term stability &amp; volatility of solvent</td>
<td>- High temp improves absorption.</td>
<td>[276]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas flow area</td>
<td>- Kₜ is controlled by the liquid film resistance even at elevated pressures.</td>
<td>- Presence of other compounds in the gas stream</td>
<td>- 20% higher performance in counter-current mode than in co-current.</td>
<td>[278]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Packing factor</td>
<td>- Kₜ can be given by Graetz-Leveque solution</td>
<td>- Compatibility of membrane and solvent.</td>
<td>- Flat sheet is better than hallow fiber membrane.</td>
<td>[294-296] [313]</td>
</tr>
<tr>
<td>GP</td>
<td>Dense membranes</td>
<td>S-P/PT, Pₑ, Pressure ratio of the permeate side to the feed side, Pore size and porosity</td>
<td>Solution-diffusion, Knudsen diffusion and molecular sieve effect are a few mechanisms.</td>
<td>Lower selectivity at higher permeability.</td>
<td>Higher gas permeability is possible with SPM.</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Hollow fiber and Flat Sheet</td>
<td>- Fick’s law to govern gas diffusion:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SLM</td>
<td>Liquid in the pores of membrane</td>
<td>T/P, Vₑ, Lₑ, Gₐ</td>
<td>- The overall mass transfer coefficient,</td>
<td>- Stability of the membrane reduces due to solvent ‘wash-out’</td>
<td>- Membrane thickness affects the gas flux.</td>
<td>[297,298]</td>
</tr>
<tr>
<td></td>
<td>Flat Sheet only</td>
<td>H₂/CO₂ selectivity and long-term stability at high T (400 °C) and P (950 psi).</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Viscosity issues arise, though ionic liquids give good capture efficiencies.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Some interesting modeling studies have been reported. They include modeling of a two stage contactor for CO₂ separation from a multicomponent gas mixture [288] and multi-stage cross and counter-current membrane contactor for CC with various process intensification and integration options with MEA as solvent [289]. Favre et al., [277] compared the performance of membrane contactors employing 1D resistance in series and, 1D and 2D convection-diffusion models for CO₂ capture with MEA as solvent. A 2D CFD model was employed to predict CO₂ capture phenomenon using PTFE and dense composite membranes. A 2D CFD model was employed [290] to predict CC phenomenon using AMP – PZ blended solvent and nanoporous membrane. Rode et al., [291] compared the simulation results with a 1D transport model for variable gas and liquid mass transfer resistances and a 2D model considering convection, diffusion and reaction contributors for a hallow fiber membrane system with MEA as solvent. The potential of N₂ selective membrane for post-combustion CC was examined [292] and optimization of energy consumption, membrane surface area and energy consumption. Very recently a simulation model was developed for CO₂ transport through a zeolite membrane and to understand the diffusion phenomenon [293]. Table 4 gives an overview of membranes based CC w.r.t the types of membranes employed, critical process parameters and major findings of the kinetic studies with challenges highlighted.
Membrane technology is successfully employed for CO2 separation from flue gases and as a contacting medium in absorption based CC. The critical parameters of any membrane based technology are selectivity and permeability and various novel membrane like mixed matrix, ionic liquids based on polymeric support are developed and used successfully in CC. Further research needs to be focused in making this technology suitable for large scale deployment.

3. Chemical looping combustion (CLC)

It is a promising energy efficient clean technology developed for CC where dilution of CO2 with flue gases is minimized. It is a flameless technology with low NOx formations. It can be treated as a second generation technology for oxy-fuel combustion based on a thermo-chemical capture process as shown in Fig. 8. The CLC is a two-step cyclic process in which the fuel (gas/liquid/solid) is burnt in the presence of metal oxides available as oxygen carriers in a fuel reactor (FR). The reduced metal oxides are then oxidized in an air reactor (AR). These metal oxides are again re-fed to the FR to complete the loop. The notable feature of this process is its inherent CC without CO2 separation. The absence of direct mixing of combustion air with the fuel makes it highly energy efficient (zero energy penalty for CO2 separation from H2O in flue gas mixture). Also, CO2 produced is not diluted with either N2 or O2. Oxygen carriers demand a higher particle residence time for the reduction reaction than for the oxidation [300,301]. The flameless nature along with its low NOx formations at lower temperatures and more importantly its inherent CO2 separation by condensation of water with minimum energy penalty are the major advantages of this technology [302–304]. The block diagram of the CLC process is given in Fig. 9 below with the working principle and the reactions involved.

Air reactor: \(\text{M}_n\text{O}_y \rightarrow 0.5\text{O}_2 \rightarrow \text{M}_n\text{O}_y\)

Fuel reactor: \((2n+m)\text{M}_n\text{O}_y + C_i\text{H}_{2m} \rightarrow (2n+m)\text{M}_n\text{O}_y-1 + m\text{H}_2\text{O} + n\text{CO}_2\)

The net reaction of the CLC: \(\text{C}_n\text{H}_{2m} + \frac{1}{2}(2n+m)\text{O}_2 \rightarrow n\text{ CO}_2 + m\text{H}_2\text{O} + \text{heat}\).

CLC (CLOU) is the 3rd generation technology of oxy-fuel combustion which is a slight modification in the CLC process but with same working principle. This concept was first developed by Lewis et al., [305] in early fifties and was re-discovered by Mattisson et al., in 2009 [306,307]. In CLOU, an oxygen carrier such as CuO/Cu2O or MnO2/Mn3O4 releases gas-phase oxygen in the fuel reactor and acts as an oxidizing agent in the air reactor. It is reported to give improved performance with solid fuels (100% capture efficiency) at a faster rate and avoids char formation. Various mixed metal oxide combinations, their synthesis protocols and operating temperatures associated with CLOU are reviewed by Mattisson et al., [308]. The enthalpy values of various metal oxides employed in the CLOU process have been reported [309]. Rydén et al., [310] employed a combination of manganese and calcium oxides. The CLOU technology has the potential to significantly reduce the residence time, reactor size and the complexity in CC. Significant research efforts are being made in recent times in the development of novel metal oxides, wide variety of fuels, reactor configurations with various energy integration options to understand the kinetics, reactor design and hydrodynamics aspects.

3.1. Significant developments

Significant developments in CLC have taken place in terms of oxygen carriers, fuels and reactor configurations during the past two decades [311–316]. Solid, liquid and gaseous fuels have been most extensively used. The gaseous fuels like syngas, natural gas, refinery gas, biogas, etc. have been employed in CLC. The critical issues of gaseous fuels are due to the presence of sulfur and light hydrocarbon impurities. They are also responsible for the reduction of the reactivity of the metal oxides and CO2 concentration in the exit stream. The selection of appropriate thermodynamically suitable metal oxides and the reactor configuration are crucial for effective operation [103,317]. CLC using solid fuels (coal, petroleum coke, solid wastes, biomass, etc.) is being widely used in the recent past and fossil fuels like coal will remain the main energy source in future too. The mechanism of solid fuel combustion follows a two-step process of gasification of solid fuel to form CO and H2 which then undergoes combustion. Another approach is the direct combustion of solid fuel with in-situ gasification by \(\text{CO}_2/\text{H}_2\text{O}\) [318–320]. The sulfur content in the fuel is a critical factor for solid fuels too and it can be tackled by integrating a desulfurizing unit along with the CLC reactor system besides selecting robust oxygen carriers that are sulfur resistant [321]. A recent review on solid fuel based CLC shows that high energy efficiency can be obtained with appropriate contactor design like ilmenite and mixed metal oxides have high reactivity, low fragmentation and attrition characteristics with high oxygen transport capacity [322]. Wood chips are also employed as solid fuel in CLC and almost complete combustion to CO2 and H2O could be achieved with 60 wt% CuO as oxygen carrier [323]. Abad et al., [324] examined various technical options to improve the CLC of solid fuels by increasing the gas--solid contact in the fuel reactor, incorporating secondary fuel reactor to reduce the unburnt compounds, recycling exhaust gases. When compared to gas and solid fuels, the literature reported on liquid fuels in CLC is relatively less. Moldenhauer et al., [325] employed kerosene (with and without sulfur) as a liquid fuel with various metal oxides in a 300 W reactor. They could achieve 99% conversion of fuel carbon to CO2.

3.1.1. Oxygen carriers

Oxygen carriers are important for a CLC system. Cho et al., [326] found Ni based metal oxide to be a better performer vis a vis other metal oxides in terms of reduction capacity but exhibited low
Factors have been made for coal fueled CLC [327]. To enhance the mechanical strength and stability, metal oxides are used with supports like Al$_2$O$_3$, TiO$_2$, ZrO$_2$, SiO$_2$, coal fly ash, etc. They are prepared by mechanical mixing, co-precipitation, freeze-granulation, spray drying and impregnation [103,328]. Ryden et al., [329] have employed perovskite and mixed metal oxides of NiO, Fe$_2$O$_3$, Mn$_3$O$_4$. They found that the perovskites are best suited for chemical loop reforming (CLR) while mixed oxides for CLC. To reduce the cost of metal oxides, natural minerals like ilmenite, bauxite waste, manganese ore and few industrial wastes like iron oxide scale, Fe–Mn slag, etc, also have been employed in the recent past with encouraging results [330–333]. Ilmenite along with NiO was found to show higher combustion efficiency than its pure form [334]. Kallen et al., [335] have very recently employed combined oxides of iron, manganese, and silica with different compositions. Ryden et al., [336] have found that composite materials like NiO or Fe$_2$O$_3$, Al$_2$O$_3$, NiAl$_2$O$_4$- or MgAl$_2$O$_4$- based supports and CaMnO$_3$ with perovskite structures demonstrated high attrition resistance. Calcium Looping (CaL) technology is now emerging as a potential and sustainable post-combustion CC option. Rapid drop in the CaO conversion in just few cycles has been the major challenge for its scale-up [337].

3.2. Reactor engineering aspects

Fixed, moving and fluidized bed contactors with single/dual circulating bubbling and spouting facilities have been used in batch and continuous modes. The typical components are fuel and air reactors, loop seal, cold traps, hydrogen generator and other auxiliary facilities [338–342]. Rotarybed reactors are employed for CLC [343]. The comparative performance of fixed and fluid contactors have been made for coal fueled CLC [345]. The superior performance of fixed bed contactor is established as far as fuel conversion and CO$_2$ concentration are concerned. However oxygen carrier particles have been found to undergo undesirable structural transformations. A novel hybrid solar thermal chemical power looping cycle is developed recently with 50% efficiency under 50% share of solar energy [346]. The commonly employed reactor configurations are shown in Fig. 10.

3.3. Kinetic and modeling studies

With the help of modeling 1D studies, Annaland et al., [344] established the desirability of a twin packed bed reactor configuration in terms of reduced oxygen carrier (OC) requirement. Markstrom et al., [347] employed a multistaged packed bed model for solid fuel based CLC with ilmenite as oxygen carrier. Ghoniem et al., [348] employed CFD modeling for oxyfuel combustion of coal. Cuadrat et al., [349] studied the nature of oxygen carrier, its porosity and the role of gasifying agents in a fluid bed reactor. Employing semi-empirical correlations, the performance of a fluid bed reactor for CLC has been simulated with ilmenite as oxygen carrier. The need for more accurate submodels has been noted. Employing heterogeneous transport modeling, predictions are made on intra-particle diffusion, temperature variations in the reaction zone and gas–solid distributions in a packed bed reactor [350]. The dynamics of a fluid bed reactor for CLC, gas composition and flow profiles, conversions encounter by the oxygen carrier and CO$_2$ capture efficiency received attention in another study [351]. Bollas et al., [352] compared various reaction schemes and kinetic mechanisms associated with CLC using methane as fuel and NiO as the oxygen carrier in a fixed bed reactor. A transient plug flow reactor model with axial dispersion has been used for simulation studies. Interestingly, shrinking core reaction model is employed to analyze the reduction reaction of NiO by CO, H$_2$ and CH$_4$. Employing CFD analysis for a hydrogen fueled reactor. The bubble hydrodynamics is studied for CaSO$_4$ as oxygen carrier [353]. Employing Reynolds averaged Navier Stokes equation, numerical simulations of oxyfuel combustion is studied [354].

Table 5 highlights the CLC contactors, oxygen carrier systems, kinetics and mass transfer informations and other details.

CLC, which is a post-combustion CC methodology, is a highly significant and upcoming technology that has huge potential in terms of energy efficiency, possible integration with power plants and inherent carbon capture feature. For commercialization of this technology, more focused studies need to be done on solid fuels in terms of identifying appropriate oxygen carriers with all the desired attributes, reactor configurations especially suitable for solid fuels and real time process conditions and accessing all possible energy integration options.

4. Cryogenic separation

Cryogenic separation of air and cryogenic distillation of carbon dioxide (−73.3 °C) has got immense industrial importance in CC. Membrane separation, adsorption and cryogenic distillation are among the novel methodologies for CO$_2$ separation. Cryogenic separation of air is known from the early 19th century onwards. Cryogenic separations suitable for high CO$_2$/H$_2$S gases in natural gas were mostly employed for off-shore applications. Some of the noted processes patented are the Ryan Holmes method (1982) [380], the controlled freeze zone (CFZ) method (1985 at Exxon Mobil Upstream Research Company) [381,382], the Cryocell

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**Fig. 10.** The reactor systems for CLC. (a) Fluidised bed; (b) Moving bed; (c) Packed bed; (d) Rotary bed.
## Table 5
Summary of chemical looping combustion based carbon capture.

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>OC, fuel type</th>
<th>Reactive Separator</th>
<th>Operating Conditions</th>
<th>CC(%)</th>
<th>Purity (%)</th>
<th>Kinetics/mass transfer</th>
<th>Challenges</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>CuO, CaO</td>
<td>3-FBR (2-CLC’s)</td>
<td>D2: 50–100 stage: 1:20 min, 20 mL/min argon saturated with H2O, stage II: at 850°C, 20 min stage III: in air for 10 min</td>
<td>85,NA</td>
<td></td>
<td>C + H2O → CO + H2, CO + H2O → CO2 + H2</td>
<td>Temperature, preparation of CuO–CaO.</td>
<td>Auto-thermal balance, H2 &amp; CO2 production simultaneously</td>
<td>[355]</td>
</tr>
<tr>
<td>coal, C3H8, iso-octane, C6H12 &amp; CH4</td>
<td>Na2SO4, CaSO4</td>
<td>TGA</td>
<td>T: 200–1200; molar ratios of carbon/Na2SO4=0.5 &amp; carbon/steam=1</td>
<td>NA,93 (with CaSO4 at 850–975°C)</td>
<td></td>
<td>Combination of iso-octane (&lt;510.58 kJ/mole) with Na2SO4 and CaSO4 produces without SO2 formation between 200°C and 344.3°C</td>
<td>The ΔH depends on the fuel but not on OC used.</td>
<td>– Na2SO4 &amp; CaSO4 are suitable.</td>
<td>[356,357]</td>
</tr>
<tr>
<td>Coal</td>
<td>Calcitic &amp; dolomitic</td>
<td>TGA</td>
<td>AR: T:25, P:0.1, V02/Na2SO4:1</td>
<td>99 (NiO at 950°C CH4 as fuel);NA</td>
<td></td>
<td>C(CuO)/CuO mole ratio of 1:1</td>
<td>Porosity favors CO2 diffusion in CaCO3 decomposition.</td>
<td>1 mole of iso-octane combustion produces 17 moles of H2–CO</td>
<td>[358–360]</td>
</tr>
<tr>
<td>Coal</td>
<td>Coal fly-ash, bauxite waste, low Ni content CaO+Al2O3</td>
<td>TGA, BFB</td>
<td>Reducing mixture of H2: H2O:N2=5:4.55:55, 200 L/min/h; Vstr: 0.1 at 900°C</td>
<td>89% at 900°C, NA</td>
<td>95% at 1000°C</td>
<td>– Lower combustion efficiency with higher OC/ fuel ratio.</td>
<td>– Char gasification in CO2 from 0.59 at 900°C to 0.65 at 1000°C</td>
<td>– fly-ash based copper oxide was favorable with high CO/H2 ratio as fuel.</td>
<td>[361–364]</td>
</tr>
<tr>
<td>Syngas, H2</td>
<td>Ilmenite, CaO, CuO on Al2O3</td>
<td>2-stage PBR-CLC</td>
<td>T: 370–1030, HR: 90–99, XOC: 80–95</td>
<td>100,NA</td>
<td></td>
<td>The packed bed of OC reduces the need of highly efficient cyclone to reduce cost; Boron Nitride(BN) used as the dense support material due to high thermal conductivity, low thermal expansion and high thermal stability.</td>
<td>PP of O2 in reactors; high solid inventories.</td>
<td>Suitable for calcium looping as a sustainable emerging technology.</td>
<td>[365–369]</td>
</tr>
<tr>
<td>Fuel Type</td>
<td>OC, fuel type</td>
<td>Reactive Separator</td>
<td>Operating Conditions P,T,C,G</td>
<td>CC亲身, Purity (%)</td>
<td>Kinetics/mass transfer</td>
<td>Challenges</td>
<td>Remarks</td>
<td>Ref</td>
<td></td>
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</tr>
<tr>
<td>CH₄, Coal</td>
<td>CuO/Cu, Iron Oxide, BN-support material as dense layer in RPBR.</td>
<td>CMBS or RPBR (1 MWth)</td>
<td>Iron Oxide: 950 °C, F₁: 1.18, CO₂ F₂: 10, D₁: 5.25</td>
<td>&gt;99, &gt;95</td>
<td>- The reduction kinetics, the activation energy parameters are critical to find fuel conversion efficiency, temperature distribution and carbon separation efficiency.</td>
<td>- Impurities in recycled flue gases; operational heat management &amp; switching valves issues.</td>
<td>- Ratio of OC (CuO) to inert alumina is 1:6 for better performance in PBR.</td>
<td>[370–375]</td>
<td></td>
</tr>
<tr>
<td>coal, kerosene, biomass</td>
<td>Ilmenite, MnO₂, MgO-ZrO₂ (40:60), CuO: ZrO₂ (20:80)</td>
<td>IFBR</td>
<td>CuO/Cu: Tₘ : 550, P₁: 15, C₃₅: 30, F₂: 1041.5, τₑₑₑₑₑₑ : 0.09, D₂ : 4.750; D₃ : 128 Uₘ : 0.0129 Φ : 0.64</td>
<td>83–99.3% at 800–950 °C, NA</td>
<td>ΔP_RC increases linearly by solid flow rate.</td>
<td>- Reaction heat exceeds the convective heat-transfer rate to the gas flow.</td>
<td>- solid fuel conversion in the condensed-size reduces the process area footprint.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄, Syngas</td>
<td>Fe₂O₃/Al₂O₃ (60:40)</td>
<td>CC-MBR</td>
<td>T: 700–975; SITC: 20–30; SFRR: 8–10 for CO SFRR: 4–12 for H₂ Fsubcrit: 1.7–2.5</td>
<td>&gt; 99%CH₄ and 100% syngas conversion. &gt; 99.99% H₂ purity.</td>
<td>ΔP_RC decreases at &gt; 6 × Uₑₑₑₑₑₑ.</td>
<td>- Higher costs due to optimum performance to char conversion with CO₂ capture.</td>
<td>Scale-up, fuel conversion, Agglomeration and attrition.</td>
<td>The volumetric gas flow in the AR must be &gt; 10 times that in the FR Suitable for iG-CLC.</td>
<td></td>
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<td>[376–379]</td>
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<td>[318–320]</td>
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<td>[323, 324]</td>
</tr>
</tbody>
</table>
method (developed by Cool Energy Ltd and tested in collaboration with Shell in Australia, Perth) [383], Twister technology (2004) [384] and the Sprex method (developed jointly by IFP, Total, and Prosernat, 2007) [385]. It has been noted by Yongliang Li [386] that separation by the cryogen occurs due to decrease in its internal energy with increase in exergy and also it can be an efficient medium to recover heat due to their low critical temperature. Oxygen is produced commercially either by cryogenic distillation process or by adsorption based processes such as VPSA.

4.1. Recent developments

In 2002, Clodic and Younes developed the cryogenic CO₂ capture process in which CO₂ was desublimated into a solid onto surfaces of heat exchangers and were cooled by evaporating a blend of refrigerants [381,387]. Pradeep Bansal (2012) [388], observed that CO₂ as a refrigerant performs significantly better than the conventional single stage refrigerants. Martin J. Tuinier et al., (2012) [389] proposed that the novel cryogenic packed-bed technology requires a 22% lower energy duty (2.9 MJ/kgCH₄ vs 3.7 MJ/kgCH₄ for the VPSA process). At a low temperature of −105 °C, the product gas leaving the packed beds reduces the cooling costs further. Cryogenic technologies operate at high pressures and low temperatures (<120 K or a liquid boils at below −150 °C) [390,391]. These systems are preferable to other conventional CC methods due to their small system size, low energy requirement, separation of acid gases in liquid form at high pressure which could be readily pumped to a reservoir [392]. The cryogenic capture process can reach 99% CO₂ capture efficiency (at 1 atmosphere) at −135 °C and 90% at −120 °C [393]. In cryogenic separation of CO₂, the moisture in feed gas should be removed in order to avoid plugging in the system. But, the major limitation of this methodology is their high capital and operating costs.

4.2. Engineering aspects

It has been reported by Takeshi Kuramochi (2012) [394] that the critical factors to be considered in cryogenic separation of CC are capacity factor (91–97%), energy prices (natural gas: €62007/GJ, coal: 2.5€2007/GJ), grid electricity: 55€/MWh, economic plant lifetime (20 years), CO₂ compression pressure (110 bar) and grid electricity CO₂ intensity (400 g/kW). In condensed rotational separation (CRS), maximum compression ratio is 4 per stage with heat exchanger effectiveness of 82% to achieve 70–90% CO₂ recovery. The energy penalty in CRS has been reported as 9–12% for an inlet CO₂ concentration of 40–70% and for CRS combined with oxygen enriched coal, combustion is 16–19% (2012) [395,396]. It is a single process of sequestration and compression. CRS separates CO₂ in liquid form with energy penalty slightly higher than gas compression alone. The inlet conditions of feed and exit conditions of product were maintained 1 bar and 40 °C in CRS. It is capable of producing waste stream purity of ≳95%CO₂ liquid at 100 bar pressure. Cryogenic combined cycles integrated with molten carbonate fuel cells (MCFC) reported with an electric efficiency similar to that of the original combined cycle (58.7% LHV). In this cell, the critical parameters are current density iₑ=1500 A/m², with cell voltage at 0.708 V and Specific Primary Energy Consumption for CO₂ Avoided (SPECCA), measured in kJLHV/kgCO₂ (2011) [397]. Annaland et al., [398] have made a techno-economic comparison between cryogenic CO₂ capture

### Table 6
Summary of cryogenic based carbon capture.

<table>
<thead>
<tr>
<th>Reactive separator</th>
<th>Operating conditions</th>
<th>CC (%), Purity of CO₂ (%)</th>
<th>Kinetics/mass transfer</th>
<th>Challenges</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS</td>
<td>MCR: 4; H₂: 82</td>
<td>≥95 at 100 atm, NA</td>
<td>The phase equilibrium model is based on equi-fugacity calculations using Peng–Robinson Equation of State, Vander Waals one-fluid mixing rules.</td>
<td>Energy penalty is 9–12% and for CRS combined with oxygen enriched coal combustion is 18–19%, 70–90% CO₂ recovery.</td>
<td>Compression with single process of sequestration.</td>
<td>[395,396] [398,399]</td>
</tr>
<tr>
<td>CCI with MCFC</td>
<td>O₉ utilization factor U₉/CO₂:11%; iₐ:1500; STCR: 3.5 at anode inlet</td>
<td>80, NA</td>
<td>SPECCA = ( \frac{100 \times \text{HRREF}}{\text{PREF}} )</td>
<td>higher CO₂ concentration on the cathode side</td>
<td>Electric efficiency is same of the original combined cycle (58.7% LHV), 22% increase in power output.</td>
<td>[397]</td>
</tr>
<tr>
<td>CASU-PB</td>
<td>O₂: 80 mol%; (inlet purity) −192 °C, 1 atm and −172 °C, 6 atm</td>
<td>90, 95</td>
<td>NA</td>
<td>Complex operating conditions of heat exchangers.</td>
<td>– Novel CPB needs &lt; 22% energy duty (2.9 MJ/kgCH₄ vs 3.7 MJ/kgCH₄ for the VPSA process)</td>
<td>[406]</td>
</tr>
<tr>
<td>DOCPB</td>
<td>Dₚ: 0.04 mm, R₉: 2.547</td>
<td>98, &gt; 99</td>
<td>( \alpha_{fi} = (1 - e_1 - e_2 + (2a_2/\gamma_1)^2 \text{RePr}^{0.45} )</td>
<td>Bed dimensions depend on cycle times.</td>
<td>– Higher energy consumption and heat leaks.</td>
<td>[407–413]</td>
</tr>
<tr>
<td>Cryogenic CO₂ Capture by FPSC</td>
<td>MFₚ=7.69; T: –20; idle operating time of 4 h, flow rate: 2 L/min; temperature of SC-1 of −20 °C.</td>
<td>&gt; 80, NA</td>
<td>( \dot{m}<em>i = h</em>{\text{inlet CO}<em>2}(\rho</em>{\text{CO}<em>2, g} - \rho</em>{\text{CO}_2, s}) )</td>
<td>Long pre-chilling time and limitation of cooling area.</td>
<td>– Energy penalty of 3.4 MJ/kg CO₂. -High efficiency, convenient to operate machine and small size.</td>
<td>[414–416]</td>
</tr>
</tbody>
</table>

- Food energy duty (2.9 MJ/kgCH₄ vs 3.7 MJ/kgCH₄ for the VPSA process)
using cooled packed beds, amine based absorption and membrane separation and found that the availability and the cost of the required utilities like LNG for the cryogenic process, steam for absorbent process determines the preferred option and the initial bed temperature, feed flow rates and CO₂ concentration in the feed are critical parameters affecting the process economics. The cryogenic capture would be best candidate for low pressure drop and simultaneous removal of various impurities in a single process. Surowtseva et al., [399] have demonstrated the combined use of hydrate and cryogenic methods at pilot level for enhanced CC for IGCC flue gases with CO₂ purity of 97% achieved in liquid form with reduced energy consumption. A novel stirling cooler system has been employed by Kitamura et al., [400] for cryogenic CC achieving the CO₂ separation from flue gas with 85% with 3.4 MJ/kg CO₂. This was found to be advantageous as the CC could be achieved at atmospheric pressure to avoid the regeneration of solvent and energy penalty of pressure drop. The long idle times and higher heat transfer resistances limiting the overall efficiency were the challenges to overcome in future research. Besides packed beds and stirling coolers, dynamically operated low cost fiber beds (with high area–volume ratio and lower sweep gas pressure drop) were successfully employed for the enhanced cryogenic CC. Two types of fiber materials were tested viz., hollow cellulose acetate and monofilament nilon were used in a two stage process achieving CO₂ purities between 28 mol% and 95.9 mol%. This would be a potential method to reduce the capital costs of the cryogenic method and to increase the CO₂ loading per chilling cycle at larger scales [401]. Kentish et al., [402] have found that by integrating membrane separation (three stages) with cryogenic separation, the cost of separation has been significantly reduced to less than $32 per ton with a feed containing 33 mol% CO₂. Berstad et al., [403] have done a critical review on the applications and the potential for low temperature CO₂ capture technologies and found that specific power consumption and the capture ratio depends on feed CO₂ concentration and that the low temperature capture was more suitable for syngas from coal gasification via a vis baseline technology. Song et al., [404] have very recently used response surface methodology (RSM) for optimization of cryogenic CC and found that the optimal conditions are fluidized-bed operation. Uniform temperature profile for the oxygen carrier is designed. Readiness with no. of cycles. Retention of advantages with scale-up is a challenge. Lower pressure drop is preferred for minimal external power intake. Agglomeration and Attrition losses affect CC efficiency. High circulation rate is required for higher capacities. 100% conversion is desired. Air leakage increases the cost of CO₂ separation. separation from flue gases. Fuel combustion capture for enhancing the sustainability of fuel combustion processes. They can be viewed as a portfolio of solutions with potential to enhance their sustainability levels further by introducing new technological solutions, renewable options and sharpening energy utilization efficiencies. The current CC options can be considered as 20–30% of the overall enhancements, the world science has to achieve. Whether any CCS technology is in transition or an end state of sustainability depends on the time frame and technology status.

The CCS technologies have to be so designed that they deliver consistent environmental and social benefits which exceed their cost of capital, energy and operation. The first level of CCS technologies have focused on the basic requirement of environment viz., GHG emission minimization for human health and safety with inherent economic tradeoffs. The second and third generation technologies will adopt more sustainable retrofits which can readily curtail the use of fossil fuels and capture agents and phase out technoeconomically inefficient process options. For example, the current option of storing CO₂ into geological

### Table 7

Comparison of various reactors used for CC.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter significance</th>
<th>Fluidized-bed</th>
<th>Moving-bed</th>
<th>Packed-bed</th>
<th>Rotary –bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas–solid contact</td>
<td>Perfect contact is essential for fast and complete operation.</td>
<td>Limited</td>
<td>Fair</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Temperature control</td>
<td>Uniform temperature profile for the oxygen carrier is designed.</td>
<td>Excellent</td>
<td>Good</td>
<td>Limited</td>
<td>Excellent</td>
</tr>
<tr>
<td>Regenerability</td>
<td>Readiness with no. of cycles.</td>
<td>Good</td>
<td>Good</td>
<td>Limited</td>
<td>Excellent</td>
</tr>
<tr>
<td>Scale-up</td>
<td>Retention of advantages with scale-up is a challenge.</td>
<td>Good</td>
<td>Fair</td>
<td>Fair</td>
<td>Excellent</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>Lower pressure drop is preferred for minimal external power intake.</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
<td>Excellent</td>
</tr>
<tr>
<td>AAP</td>
<td>Agglomeration and Attrition losses affect CC efficiency.</td>
<td>Very high medium</td>
<td>Very high medium</td>
<td>Limited</td>
<td>Limited</td>
</tr>
<tr>
<td>Oxygen carrier circulation</td>
<td>High circulation rate is required for higher capacities.</td>
<td>Good</td>
<td>Fair</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Fuel conversion</td>
<td>300% conversion is desired.</td>
<td>Good</td>
<td>Fair</td>
<td>Fair</td>
<td>Excellent</td>
</tr>
<tr>
<td>Gas leakage</td>
<td>Fair</td>
<td>OFC-II, OFC-III, SAFB</td>
<td>OFC-II, OFC-III</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ separation</td>
<td>Air leakage increases the cost of CO₂ separation. separation from flue gases</td>
<td>Post-CCC,OFCC-I</td>
<td>Post-CCC</td>
<td>Post-CCC &amp;pre-CCC</td>
<td>Post-CCC,OFCC-II, OFC-III</td>
</tr>
</tbody>
</table>

**Note:** AAP: agglomeration and attrition of particles.
forms has to be transient solution since public opposition and concerns about global climate change have to be met in due course of time.

Viewed from the above context, the current and future developments in CC technologies have also to be explained from sustainability consideration. The CO₂ capture by the absorption, adsorption or membrane separation if used in conjunction with CO₂ utilization processes like urea, precipitated CaCO₃, CO and methanol generation will significantly nullify the energy penalties associated with the CC process. They become more sustainable from energy and material utilization viewpoints. Enhanced oil recovery with captured CO₂ will enable its large scale utilization at transition option. Tables 7 and 8 show comparison of reactors used in CC and critical comparison of CC technologies respectively.

Various carbon capture technologies discussed above may be employed for pre- or post-combustion CC or both. The critical comparison of all these technical options has been provided in Table 7 with reference to classification of the CCT, conventional and novel materials employed, contactor configurations used to achieve the objective, maximum CC achieved, important models and scale-up challenges.

Critical comparison of technologies.

<table>
<thead>
<tr>
<th>CCT</th>
<th>Type</th>
<th>Conventional methods</th>
<th>Novel methods</th>
<th>CC (η) (max. achieved)</th>
<th>Reactors</th>
<th>Kinetic modeling and simulation</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbent</td>
<td>Pre-CCC, Post-CCC</td>
<td>Single solvents as piperazine, binding organic liquids, MEA, K₂CO₃, DIPA, MDEA, etc.</td>
<td>Mixed solvents as MEA + K₂CO₃, AMP-PZ, PEI-SiO₂, Alcoholamine/ H₂O, DEA-MDEA, MEA-DEA</td>
<td>100</td>
<td>PBR, Double stirred cell, bubble column, rotating packed bed, tray towers</td>
<td>NLP model, absorber Sorbent flow characteristics and kinetics</td>
<td>Solvent selection and reactor type</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>Post-CCC</td>
<td>Viscose Rayon + HCM, ZK + MEA, NaX, Flyash + PEI + PEG, Uio66-MOF</td>
<td>Flyash + PEI + PEG, Co-MOF-74(MS), CaO (CLP), PEI + MCM-41, PEI-silicagel, amine silica aerogel, FAC</td>
<td>95</td>
<td>SAFB, PBR (TSA, PSA and ESA), RPB</td>
<td>Langmuir adsorption isotherm, Eulerian–Lagrangian model, Toth and dual site Langmuir isotherms, Molecular and Knudsen diffusion, ZLC technique, fluidized bed contactor performance equations of motion, One-dimensional, two-dimensional model and convection-diffusion, Regenerator height and multiphase CFD flow</td>
<td>Faster synthesis with MS and enhanced capacity with KOH &amp; NaOH</td>
</tr>
<tr>
<td>Membrane</td>
<td>Post-CCC</td>
<td>Micro-porous membrane</td>
<td>Liquid in pores of membrane and dense membranes, DEA supported on polyvinyl alcohol, ionic liquids supported on PVDF, polymers, etc</td>
<td>100</td>
<td>Hollow fiber and Flat Sheet membrane packed columns</td>
<td></td>
<td>Viscosity with ionic membrane</td>
</tr>
<tr>
<td>OFC(OFC-I)</td>
<td>OFC</td>
<td>ASU for pure O₂ mixed with recycle CO₂</td>
<td>35%O₂, 65%CO₂ and sand particles for enhanced combustion</td>
<td>100</td>
<td>FBR, PBR</td>
<td>Gas composition and load generation models, Adaptation of non-linear control gains, turbine system control gains, turbine Adaption of non-linear load generation models, turbine system control gains, turbine</td>
<td>Inventory and scale-up</td>
</tr>
<tr>
<td>CLC(OFC-II)</td>
<td>OFC</td>
<td>NiO, CuO, Mn₃O₄, Fe₂O₃, etc.</td>
<td>MOF, CaO supported on cement</td>
<td>&gt; 99</td>
<td>RPBR, CBFR, PBR</td>
<td>Hydrodynamic, Heat transfer and mass transfer models, 3-CLC reactors for NH₃ synthesis, 1D &amp; 2D reactor models, large eddy simulations.</td>
<td>Inventory, attrition, agglomeration and scale-up</td>
</tr>
<tr>
<td>CLOU(OFC-III)</td>
<td>OFC</td>
<td>CoO, Mn₃O₄, CuO, etc.</td>
<td>CuO supported on Mg-Al₂O₃, i-CLC for in-situ gasification of solid fuels with suitable OC</td>
<td>100</td>
<td>RPBR</td>
<td>Mass transfer and heat transfer models, Partial pressures of O₂ in oxidation and reduction reaction rates, 1D &amp; 2D reactor models, large eddy simulations.</td>
<td>Inventory, agglomeration and scale-up</td>
</tr>
<tr>
<td>Algae systems</td>
<td>Bio-sequestration</td>
<td>Algae in open pond cultivation</td>
<td>Algae in bio reactors</td>
<td>100</td>
<td>BESS, MEDC, BR-MPBR</td>
<td></td>
<td>Inventory and scale-up 16–19% Energy penalty</td>
</tr>
<tr>
<td>Cryogenic CO₂ separation</td>
<td>Cryogenic CO₂ capture</td>
<td>Cryogenic chillers, Heat exchangers</td>
<td>CCI with MCFPC, FPSC</td>
<td>100</td>
<td>PBR, Stirring cooler</td>
<td>Based on equ-fugacity model, frosted CO₂ depends on heat transfer between gas stream and cooling fins</td>
<td></td>
</tr>
</tbody>
</table>
options have been comprehensively reviewed w.r.t. material development, process and engineering aspects including contactors/reactor configurations and their design aspects along with successful models developed to explain the process performance. This review shows that the tremendous global knowledge base available in this area and a portfolio of alternative technologies exists now though at different technology readiness levels. Some of them have passed laboratory, bench and pilot plant stages of development they need to be demonstrated on a larger scale. At this juncture, no technology may be a credible candidate by itself for commercial level implementation. However, the portfolio as a whole is large enough to throw several commercially viable alternatives in the future.

The post-combustion capture of CO₂ from industrial flue gases through gas–liquid absorption need high level R&D with focus on evolving cost effective desorption option. At present, it is the only industrial carbon emission management technology that has very high potential for wide scale deployment. The large scale storage of CO₂ is not a long term solution. The commercial success of CCS technologies to a great extent depends on CO₂ utilization to generate industrial chemicals of high commercial value. Intense R&D is required in this area. The largest deployment of CC technologies has to occur in developing countries in the coming years and CO₂ utilization will be an important component of their effort to combat climate change.

Dedication

This paper has been gratefully dedicated to our beloved teacher, “Dr. K.V. Raghavan” who has been our constant source of inspiration, enthusiasm and support on the eve of 50 years of illustrious research career completion on 1/10/2014.

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