

# Carbon Dioxide Capture and Storage: A General Review on Adsorbents

Mohammad Songolzadeh , Maryam Takht Ravanchi , Mansooreh Soleimani

**Abstract**—CO<sub>2</sub> is the primary anthropogenic greenhouse gas, accounting for 77% of the human contribution to the greenhouse effect in 2004. In the recent years, global concentration of CO<sub>2</sub> in the atmosphere is increasing rapidly. CO<sub>2</sub> emissions have an impact on global climate change. Anthropogenic CO<sub>2</sub> is emitted primarily from fossil fuel combustion. Carbon capture and storage (CCS) is one option for reducing CO<sub>2</sub> emissions. There are three major approaches for CCS: post-combustion capture, pre-combustion capture and oxyfuel process. Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them.

There are several post combustion gas separation and capture technologies being investigated, namely; (a) absorption, (b) cryogenic separation, (c) membrane separation (d) micro algal bio-fixation and (e) adsorption. Apart from establishing new techniques, the exploration of capture materials with high separation performance and low capital cost are paramount importance. However, the application of adsorption from either technology, require easily regenerable and durable adsorbents with a high CO<sub>2</sub> adsorption capacity. It has recently been reported that the cost of the CO<sub>2</sub> capture can be reduced by using this technology. In this paper, the research progress (from experimental results) in adsorbents for CO<sub>2</sub> adsorption, storage, and separations were reviewed and future research directions were suggested as well.

**Keywords**—Carbon capture and storage, pre-combustion, post-combustion, adsorption

## I. INTRODUCTION

CARBON dioxide is the major greenhouse gas, which is the largest contributor to global warming. The emission of carbon dioxide to the atmosphere has been identified as a major contributor to global warming [1-4]. Sources of carbon dioxide are divided into two categories: natural source and human source.

Natural sources of carbon dioxide are more than 20 times greater than sources due to human activity, but over periods longer than a few years natural sources are closely balanced by natural sinks [3]. Main human source is the combustion of fossil fuels such as coal, natural gas or petroleum, and industrial processes such as power plants, oil refining and the production of cement, iron and steel [4-7]. Carbon dioxide has been already used in petrochemical industries for production of limited chemicals such as urea [1].

Since the beginning of the industrial age in ca. 1800, the CO<sub>2</sub> concentration in atmosphere has increased from 280 to 390 ppm in 2010 [8-9]. Carbon capture and storage (CCS) will play a crucial role to attain the required greenhouse gas (GHG) emissions reduction [10].

M.Songolzadeh is with Amirkabir University of Technology, No.424, Hafez Ave., Tehran, Iran, (e-mail: songol8571013@aut.ac.ir).

M. Takht Ravanchi is with Petrochemical Research and Technology co. Iran, (e-mail: maryamravanchi@gmail.com)

M.Soleimani is with Amirkabir University of Technology, No.424, Hafez Ave., Tehran, Iran, (Tel. & Fax: +98(21) 66405847; E-mail: Soleimanim@aut.ac.ir

CCS can be defined as the separation and capture of CO<sub>2</sub> produced at stationary sources, followed by transport and storage in geological reservoirs or the ocean [11-12]. There are three major approaches for CCS: post-combustion capture, pre-combustion capture and oxyfuel process.

In pre-combustion, the fossil fuel is reacted with air or oxygen and is partially oxidized to form CO and H<sub>2</sub> (syngas). Then in a gasification reactor, it is reacted with steam to produce a mixture of CO<sub>2</sub> and more H<sub>2</sub>. CO<sub>2</sub> is then separated, and resulting in a hydrogen-rich fuel which can be used in many applications. Oxy-combustion is when oxygen is used for combustion instead of air, which results in a flue gas that consists mainly of pure CO<sub>2</sub> and is potentially suitable for storage. The post combustion capture is based on removing CO<sub>2</sub> from flue gas after combustion. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates/captures most of the CO<sub>2</sub> [3, 13-14].

Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them. This makes post-combustion capture easier to implement as a retrofit option (to existing power plants) compared to the other two approaches. Therefore, post-combustion capture is probably the first technology that will be deployed [15].

Among the various separation technologies such as absorption, adsorption, cryogenic, membrane and micro algal bio-fixation, adsorption may be considered as a competitive solution. Its major advantage is the ease of the adsorbent regeneration by thermal or pressure modulation [3, 14, 16].

Flue gases of current power plants are a mixture of nitrogen, oxygen, carbon dioxide, SO<sub>2</sub>, NO<sub>x</sub> and water plus other minor contaminants [12, 14]. The concentration of CO<sub>2</sub> in the flue gas is typically only 10–15% (around 12%) depending on the fuel used [17-18]. Flue gases are normally at atmospheric pressure but the temperatures might be between 320 K and 400 K, depending on the extent and type of contaminant removal [19]. The flue gas conditions have created many problems for CO<sub>2</sub> capture.

In addition to cryogenic process, absorption and membrane technology, adsorption is a separation technology, potential to reduce the cost and energy of post-combustion capture compared to other technologies. Adsorption processes for gas separation via selective adsorption on solid media are also well-known, and it can produce high purity streams with low energy consumption [5, 10, 20-23].

## II. ADSORPTION

Adsorption is a physical process that involves the attachment of a gas or liquid to a solid surface. Adsorption can reduce energy and cost of the capture or separation of CO<sub>2</sub> in post-combustion capture. However, the success of this approach is dependent on the development of an easily regenerated and durable adsorbent with high CO<sub>2</sub> selectivity and adsorption capacities [1-4].

In general, the CO<sub>2</sub> adsorbent must have high selectivity and adsorption capacity, adequate adsorption/desorption kinetics, remain stable after several adsorption/desorption cycles, and possess good thermal and mechanical stability [17, 24].

Adsorbents which could be applied to CO<sub>2</sub> capture include activated carbons, carbon fibres, silica gel, ion-exchange resins, zeolites, and porous silicates (SBA-15, MCM-41, etc.), activated alumina, metal oxides (CaO, MgO, K<sub>2</sub>O, Li<sub>2</sub>O), metal-organic frameworks (MOFs), organic-inorganic hybrid sorbents and other surface-modified porous media. However, zeolites, porous silica, and MOFs show negligible CO<sub>2</sub> adsorption at high temperature [9, 15, 25-26]. The adsorbents are used for CO<sub>2</sub> capture placed into two categories: physical and chemical adsorbents.

#### A. Chemical Adsorption

Chemisorption is a sub-class of adsorption, driven by a chemical reaction occurring at the exposed surface. Chemical adsorbents are mostly metal compounds. Metal compounds in two forms are used for CO<sub>2</sub> adsorption: metal oxides and metal salts. A wide range of metals have been studied, metal oxides (e.g. CaO, MgO, etc.), lithium metal oxides (e.g. Li<sub>2</sub>ZrO<sub>3</sub>, Li<sub>4</sub>SiO<sub>4</sub>, etc.), metal salts from alkali metal compounds (i.e. lithium silicate, lithium zirconate) to alkaline earth metal compounds (i.e. magnesium oxide and calcium oxide), hydrotalcites and double salts [24, 27].

In general, one mole of metal compound can react with one mole of CO<sub>2</sub> with a reversible reaction [27]. The process consists of a series of cycles where metal oxides (such as CaO) at 650 °C are transformed into metal carbonates form (such as CaCO<sub>3</sub>) at 850°C in a carbonation reactor, and then decarbonated in a decarbonation reactor allows to regenerate the sorbent and to produce a concentrated stream of CO<sub>2</sub> suitable for storage [28-29].

Considerable attentions were paid to calcium oxide (CaO) as it has a high CO<sub>2</sub> absorption capacity and high raw material availability (e.g. limestone) at a low cost. Lithium salts recorded a good performance in CO<sub>2</sub> absorption, but it gained less focus due to its high production cost [27].

Hydrotalcite (HT) contains layered structure with positively charged cations and is balanced by negatively charged anions. HTI-K-Na adsorbed CO<sub>2</sub> at 1.109 mol/kg under wet condition at 300 °C and total pressure of 1.34 bar (CO<sub>2</sub> partial pressure of 0.4 bar). The measured loss of capacity was only 6.7% after 50 cycles of operation [24].

Although double salts can be easily regenerated due to low energy requirement, their stability has not been investigated. The long-term stability and performance of alkali metal-based sorbents under actual flue gas conditions remains to be established [27-28].

One way for improving adsorption efficiency is using nanomaterials for CO<sub>2</sub> adsorption. Nanomaterials are materials with at least one dimension equals or less than 100 nm [27]. The nanocrystalline Li<sub>2</sub>ZrO<sub>3</sub> achieved 27 wt% absorption capacity in 5 min compared to the normal Li<sub>2</sub>ZrO<sub>3</sub> that need 24h to achieved 18 wt% adsorption capacity. The sorbent was also more stable in CO<sub>2</sub> adsorption/desorption process and maintained the capturing capacity after 7 cycles.

Essaki et al [30] investigated flue gas removal using packed-bed lithium silicate pellets. CO<sub>2</sub> adsorption capacity was reported 5.0 (mol CO<sub>2</sub>/kg sorbent at 600 °C) which was relatively low compare to the lithium silicate nanoparticles [27].

However, nanomaterials are always related to high production cost with complicated synthesis process. The disadvantages of chemical adsorbents are difficult regeneration, and usage of these adsorbents need more studies for finding new adsorbents.

#### B. Physical Adsorption

Physisorption, also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption.

The major physical adsorbents reported for CO<sub>2</sub> adsorption include activated carbons, inorganic porous materials such as zeolites, hydrotalcites [4, 9, 28, 31]. If the CO<sub>2</sub> adsorption capacity of solid adsorbents reaches 3 mmol/g, the required energy for adsorption will be less than 30–50 % energy for absorption with optimum aqueous mono-ethanolamine (MEA) [32].

Coal is one of the adsorbent suggested for CO<sub>2</sub> capture. Sakurovs et al. [33] found an approximately proportional relationship between the maximum sorption capacity of a coal for gases and their critical temperature. The critical temperature of carbon dioxide is greater than methane; therefore carbon dioxide is adsorbed more strongly than methane on the coal.

Results of Sakurovs et al. [33] showed that the ratio of maximum sorption capacity between carbon dioxide and methane decreases with increasing carbon content. The average CO<sub>2</sub>/CH<sub>4</sub> sorption ratio is higher for moisture-equilibrated coal and decreases with increasing coal rank [34].

The total amount of CO<sub>2</sub> that can be adsorbed in coal depends on its porosity, ash and affinity for this molecule. Ratios between CO<sub>2</sub> and CH<sub>4</sub> adsorption capacities vary from 1.4 for high rank coals to 2.2 for low rank coals [8].

Activated carbon (AC) has a number of attractive characteristics, such as its high adsorption capacity, high hydrophobicity, low cost, and low energy requirement for regeneration [35]. Activated carbons present a series of advantages as CO<sub>2</sub> adsorbents: they are inexpensive, insensitive to moisture, has high CO<sub>2</sub> adsorption capacity at ambient pressure and, moreover, they are easy to regenerate, and they have well developed micro and mesoporosities [10, 22, 27, 36].

Siriwardane et al. [37] studied the adsorption of CO<sub>2</sub> on the molecular sieve 13X, 4A and activated carbon. The molecular sieve 13X showed better CO<sub>2</sub> uptake than molecular sieve 4A. At lower pressures activated carbon had a lower CO<sub>2</sub> uptake than the uptakes of the molecular sieves, but at higher pressures the adsorption was higher for activated carbon than molecular sieves [37].

However, activated carbon CO<sub>2</sub>/N<sub>2</sub> selectivities (ca. 10) are relatively low. Zeolitic materials, on the other hand, offer CO<sub>2</sub>/N<sub>2</sub> selectivities 5-10 times greater than those of carbonaceous materials [28].

The capacity of NaKA zeolite to adsorb CO<sub>2</sub> was similar to the capacity of NaA zeolite, 3.88 mmol/g. A very high ideal CO<sub>2</sub>/N<sub>2</sub> selectivity (172 times) and a high CO<sub>2</sub> adsorption capacity (3.2 mmol/g) were observed at an optimal K<sup>+</sup> content of 17 atoms% rendering NaKA [38].

In physical adsorption, the size and volume of the pores are important. Micropores are defined as pores, 2 nm in size, mesopores between 2 and 50 nm, and macropores, 50 nm in size. The micropores make better selective adsorption of CO<sub>2</sub> over CH<sub>4</sub> [26, 39-41].

Carbon nanotubes (CNTs) are most famous among nano-hollow structured materials with their dimension ranges from 1 to 10 nm in diameter and 200 to 500 nm in length. Cinke et al. investigated purified single-walled carbon nanotubes (SWNTs) adsorbed CO<sub>2</sub> better than unpurified SWNT. In addition, Multi-walled carbon nanotubes (MWCNTs) showed stability for 20 cycles of adsorption and regeneration [27]. Lu et al. compared the adsorption capacity of MWCNTs with granular activated carbon (GAC) and zeolite. Under the same adsorption condition, MWCNTs recorded CO<sub>2</sub> adsorption capacity as 1.57 mol CO<sub>2</sub>/kg sorbent while activated carbon and zeolites adsorbed 1.65 mol CO<sub>2</sub>/kg sorbent and 1.44 mol CO<sub>2</sub>/kg sorbent, respectively [27].

Incorporation of multi walled carbon nanotube (MWCNT) into HKUST-1, [Cu<sub>3</sub>(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)<sub>2</sub> (H<sub>2</sub>O)<sub>3</sub>·xH<sub>2</sub>O, (Cu<sub>3</sub>(btc)<sub>2</sub>; btc = 1,3,5- benzene-tricarboxylate) have been reported by Zhonghua et al. [42]. Unmodified [(Cu<sub>3</sub>(btc)<sub>2</sub>] and [CNT@Cu<sub>3</sub>(btc)<sub>2</sub>] have showed CO<sub>2</sub> capacity of 295 and 595 mg /g, at 298 K and 18 bar, respectively. MIL-101 or Cr<sub>3</sub>(F,OH)(H<sub>2</sub>O)<sub>2</sub>O[(O<sub>2</sub>C)C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>)<sub>3</sub>·nH<sub>2</sub>O (n ≈ 25), is one of the metal organic framework with Lewis acid sites that can be activated by removal of guest water molecules. Anbia and Hoseini [31] have incorporated MWCNTs into MIL- 101 to synthesize a hybrid composite and denoted it as MWCNT@MIL-101. MIL-101 and MWCNT@MIL-101 show CO<sub>2</sub> adsorption capacities of 0.84 and 1.35 mmol/g at 298 K and 10 bar, respectively (CO<sub>2</sub> adsorption capacity enhanced about 60%) [31].

Liu et al. indicated that zeolite 5A has higher volumetric capacities and less heat effect of the zeolite 13X [43]. Chabazite zeolites were prepared and exchanged with alkali cations – Li, Na, K and alkaline-earth cations – Mg, Ca, Ba, were studied to assess their potential for CO<sub>2</sub> capture from flue gas by vacuum swing adsorption. It was found that NaCHA and CaCHA hold comparative advantages for high temperature CO<sub>2</sub> separation whilst NaX showed superior performance at relatively low temperatures [44].

The average values of heat adsorption on zeolites (36 kJ/mol) is larger than for AC (30 kJ/mol), confirming the mentioned affirmation. Moreover, this carbon was easily regenerated completely and it did not shown capacity decay after 10 consecutive cycles [10].

The presence of several impurity gases (SO<sub>x</sub>/NO<sub>x</sub>/H<sub>2</sub>O) greatly complicates the CO<sub>2</sub> separation processes. Therefore, conventional adsorption-based CO<sub>2</sub> capture processes rely on using a pre-treatment stage to remove water, SO<sub>x</sub> and NO<sub>x</sub>, which adds considerably to the overall cost [23].

Yi et al. showed that the adsorption capacities follows the order SO<sub>2</sub> > CO<sub>2</sub> > NO > N<sub>2</sub> on both zeolites (5A and 13X). Compare two different adsorbents, the better separation efficiency can be realized by 5A zeolite [45].

Due to the increase cost of raw materials, growing research interest has been focused on producing AC from agricultural waste. Some of the agricultural wastes include the shells and stones of fruits, wastes resulting from the production of cereals, bagasse and coir pith [46]. Rosas et al. prepared hemp-derived AC monolith by phosphoric acid activation.

The porosity of ACs derived from hemp stem is highly depended on the activation temperature, whereas the activation time has a minor influence. The hemp stem derived carbons are microporous materials and therefore suitable materials for hydrogen storage and CO<sub>2</sub> capture [46].

More recently, nano-systems researchers have synthesized and screened a large number of zeolitic-type materials known as zeolitic imidazolate frameworks (ZIFs). CO<sub>2</sub> capacities of the ZIFs are high, and selectivity against CO and N<sub>2</sub> is good. As there is a great deal of flexibility in the kinds of ZIF structures that can be synthesized, it is likely the new materials with even better adsorption selectivity and capacity can be developed in this way [28].

Recently, gas adsorption by activated carbon fibres and carbon fibre composites has been identified as a promising alternative. Lately, structured porous monolith materials made from carbon fibres, which have the ability to selectively adsorb. The results of some researchers (Burchell and Judkins, Dave et al., Yong et al.) indicate that the CO<sub>2</sub> adsorption efficiency of the honeycomb monolith is twice that of activated carbon and 1.5 times greater than ZIF material [3].

Alcaniz-Monge et al. [47] studied CO<sub>2</sub> adsorption performance on a honeycomb adsorbent made from cellulose and pitch. Petroleum pitch-1 based honeycomb monolithic composite captured 97% of CO<sub>2</sub> present. Kimber et al. indicated the selectivity of CO<sub>2</sub> decreased with increase in burn-off [3].

Metal-organic framework (MOF) materials are crystalline with two- or three-dimensional porous structures that can be synthesised with many of the functional capabilities of zeolites.

They are formed due to the coordination bonds between metal salt and multidentate ligands. MOFs are promising candidates as separation materials for CO<sub>2</sub> capture [5-6, 9, 31, 41].

Several MOFs have been proposed as adsorbents for CO<sub>2</sub> separation processes, and among these Cu-BTC [polymeric copper(II) benzene- 1,3,5-tricarboxylate] proved to be endowed with CO<sub>2</sub> adsorption performances that are higher than those of typical adsorbents such as 13X zeolite [48].

Millward and Yaghi [49] investigated CO<sub>2</sub> isotherms for a cross-section of framework characteristics such as square channels (MOF-2), pores decorated with open metal sites (MOF-505 and Cu<sub>3</sub>(BTC)<sub>2</sub>), hexagonally packed cylindrical channels (MOF-74), interpenetration (IRMOF-11), amino- and alkyl-functionalized pores (IRMOFs-3 and -6), and the extra-high porosity frameworks IRMOF-1 and MOF-177.

Their results indicated that adsorption capacities of CO<sub>2</sub> varies from 3.2 mmol/g for MOF-2 to 33.5 mmol/g for MOF-177 at ambient temperature and pressure of 45 bar [41].

Zirconium-metal organic frameworks (Zr-MOFs) were synthesized with or without ammonium hydroxide as an additive in the synthesis process.

Adsorption tests showed that Zr-MOF presented much higher CO<sub>2</sub> adsorption than CH<sub>4</sub>. Zr-MOF exhibited CO<sub>2</sub> and CH<sub>4</sub> adsorption of 8.1 and 3.6 mmol/g, respectively, at 273 K, 988 kPa [41].

Zhang et al. focused on the effect of water vapour on the pressure/vacuum swing adsorption process. The selected adsorbents in this study were CDX (an alumina/zeolite blend), alumina and zeolite 13X as these adsorbents will be either the pre-layer for water adsorption or the main CO<sub>2</sub> adsorption layer in the packed bed [23].

The MCM-41 material is one of the mesoporous products made by the hydrothermal method. Lu et al. showed the mesoporous silica spherical particles (MSPs) can be synthesized using low-cost Na<sub>2</sub>SiO<sub>3</sub>, thus they can be a cost-effective adsorbent for CO<sub>2</sub> greenhouse gas capture from flue gas [6, 50].

The adsorption capacities of various zeolite adsorbents are summarized in Table I.

TABLE I  
CO<sub>2</sub> ADSORPTION CAPACITIES OF DIFFERENT ZEOLITES [5].

Zeolite type	T [K]	p <sub>CO2</sub> [bar]	q [mmol.g <sup>-1</sup> ]	Cycle
13 X	393	0.15	0.7	-
5 A	393	0.15	0.38	-
4 A	393	0.15	0.5	-
WEG-592	393	0.15	0.6	-
APG-II	393	0.15	0.38	-
Na-Y	273	0.1	4.9	-
Na-X	373	1	1.24	2
NaX-h	323	1	2.52	2
NaX-h	373	1	1.37	2
Na-X-c	323	1	2.14	2
Na-X-c	373	1	1.41	2
Cs-X-h	323	1	2.42	2
Cs-X-h	373	1	1.48	2
Cs-X-c	323	1	1.76	2
Cs-X-c	373	1	1.15	-

Layered double hydroxides (LDHs) have the general formula  $[M_{1-x}^{II}M_x^{III}(OH)_2][X_q^{n-}.nH_2O]$  with x typically in the range between 0.10 and 0.33. These materials can be readily and inexpensively synthesized with the desired characteristics for a particular application. A CO<sub>2</sub> adsorption capacity of 3.55 mmol g<sup>-1</sup> was achieved by Ca-Al LDH with ClO<sub>4</sub><sup>-</sup> anion at 330 °C and 1 bar [32].

Graphite nanoplatelets (GNP) were prepared by acid intercalation followed by thermal exfoliation. Functionalized graphite nanoplatelets (f-GNP) were prepared by further treatment of GNP in acidic medium.

Palladium (Pd) nanoparticles were decorated over f-GNP surface by chemical method. Results of Mishra et al. were showed that maximum adsorption capacities of Pd-GNP nanocomposite and f-GNP (at 25 °C and 11 bar) were 0.0051 and 0.0043 mol/g, respectively, (at 50 °C and 11 bar) were 0.0045 and 0.0038 mol/g, and although (at 100 °C and 11 bar) were 0.0041 and 0.0033 mol/g [51].

### C. Adsorbent Modification

The role of CO<sub>2</sub> as a weak Lewis acid is well established. According to the nature of carbon dioxide, the surface of the physical adsorbents can be modified by adding basic groups, such as amine groups and metal oxides [26, 28, 36, 40]. Three different methods for production of these adsorbents were investigated: activation with carbon dioxide, heat treatment with ammonia gas (amination and ammoxidation) and heat treatment with polyethylenimine (PEI) [7, 22, 36]. However, it has been suggested that amine modification can produce better and cheaper CO<sub>2</sub> adsorbents. Recently, the improvement of the adsorptive properties of activated carbons using metallic species, such as copper oxides, has been reported to be effective for carbon dioxide adsorption [40, 52].

The templated type of activated carbons exhibit a high CO<sub>2</sub> adsorption rate, a good adsorption capacity (~ 3.2 mmol CO<sub>2</sub>/g at 25 °C), a good selectivity for CO<sub>2</sub>/N<sub>2</sub> separation (~ 6.5) and they can easily be regenerated [26]. Furthermore, unlike typical commercial adsorbents such as zeolites, TRI-PEMCM-41 is tolerant to moisture in the feed and is highly selective towards acid gases in mixtures with nitrogen, oxygen, hydrogen and methane even at very low concentrations [7, 53].

Possible techniques for enhancing the adsorption capacity include loading amines onto various types of supports such as mesoporous silicas, including SBA-12 (Zelenak et al.), SBA-15 (Hiyoshi et al.; Zelenak et al.; Zukal et al.), microspheres (Araki et al.). Alternative supports include zeolites (Su et al.; Zukal et al.), MCM-41 (Zelenak et al.) and MCM-48 (Huang et al.; Kim et al.) [32].

Xu et al. designed selective 'molecular basket' by grafting poly-ethylenimine (PEI) uniformly on MCM-41. CO<sub>2</sub> adsorption capacity of the sorbent was 24 times higher than MCM-41 and 2 times higher than PEI [27].

The addition of ammonium hydroxide resulted in the Zr-MOF with a slight lower adsorption of CO<sub>2</sub> and CH<sub>4</sub>, however, the selectivity of CO<sub>2</sub>/CH<sub>4</sub> is significantly enhanced. Results of Abid et al. showed the selectivity of CO<sub>2</sub>/CH<sub>4</sub> on Zr-MOF is between 2.2 and 3.8, while for Zr-MOF-NH<sub>4</sub> selectivity is between 2.6 and 4.3 [41].

A nitrogen-rich carbon with a hierarchical micro-mesopore structure exhibited a high CO<sub>2</sub> adsorption capacity (141 mg/g at 25 °C, 1 atm), excellent separation efficiency (CO<sub>2</sub>/N<sub>2</sub> selectivity is ca. 32) and excellent stability [53].

Amine modified layered double hydroxides (LDHs) have been prepared by several different methods. Park et al used dodecyl sulfate (DS) intercalated LDH as precursor and added (3-aminopropyl) triethoxysilane (APTS) together with N-cetyl-N,N,N-trimethylammonium bromide (CTAB). Wang et al. [32] investigated the synthesis of amine modified layered double hydroxides (LDHs) via an exfoliation and grafting synthetic route is reported. The highest adsorption capacity for CO<sub>2</sub> was achieved at 1.75 mmol/g by MgAl N<sub>3</sub> at 80 °C and 1 bar [32].

Meng et al. [25] reported that porous carbons with well-developed pore structures were directly prepared from a weak acid cation exchange resin (CER) by the carbonization of a mixture with Mg acetate in different ratios.

The porous carbons exhibited the highest CO<sub>2</sub> adsorption values of 164 mg/g at 1 bar and 1045 mg/g at 30 bar.

The adsorbents were prepared based on the central composite design (CCD) with three independent variables (i.e., amination temperature, amination time, and the use of pre-heat treated (HTA) or pre-oxidized (OXA) sorbent as the starting material). Shafeeyan et al. demonstrated that the optimum conditions for obtaining an efficient carbon dioxide adsorbent is usage of a pre-oxidized sorbent and amination at 425 °C for 2.1 h [35].

Gargiulo et al. showed CO<sub>2</sub> adsorption capacity of PEI-functionalized TUD-1 (Technische Universit t Delft) silica is about 3 mmol/g, if not better than those relative to similar substrates [48].

Jang et al. [40] studied the adsorption behaviours of nickel oxide loaded activated carbons for CO<sub>2</sub> capture. The maximum CO<sub>2</sub> adsorption capacity was found to be 49.9 cm<sup>3</sup>/g at the 10 min-NiO-ACs that is higher than ACs of 41.2 cm<sup>3</sup>/g at 25 °C.

Table III compares CO<sub>2</sub> adsorption capacities and stability of different adsorbents, which were studied for post-combustion CO<sub>2</sub> capture.

### III. DIFFERENT CYCLE FOR CO<sub>2</sub> ADSORPTION

Four different regeneration strategies were compared in a single-bed CO<sub>2</sub> adsorption unit: pressure swing adsorption (PSA), temperature swing adsorption (TSA), vacuum swing adsorption (VSA), electric swing adsorption (ESA) and a combination of vacuum and temperature swing adsorption (VTSA).

For the single-bed cycle configurations, the productivity and CO<sub>2</sub> recovery followed the sequence:

$$ESA < TSA < PSA < VSA < VTSA.$$

Values of productivity up to 1.9 mol kg<sup>-1</sup> h<sup>-1</sup> and a maximum CO<sub>2</sub> recovery of 97% were reached [10, 20, 48]. The performances found in the literatures of PSA, VSA and ESA processes for CO<sub>2</sub> capture are reported in Table II.

### IV. CONCLUSION

CO<sub>2</sub> emissions have an impact on global climate change. Many various technologies such as membrane separation, absorption, cryogenic distillation and adsorption can be used for CO<sub>2</sub> capture. The adsorption is the ideal way to achieve efficient CCS. Conventional solid adsorbents include activated carbons, zeolites, ion-exchange resins and meso-porous silicates, activated alumina, metal oxides, and other surface-modified porous media.

In this work, the application and efficiency of different adsorbents were compared together. It can be concluded that the choice of the best adsorbent depends on the operating conditions of the process. The CaO-MgAl<sub>2</sub>O<sub>4</sub> and nano CaO/Al<sub>2</sub>O<sub>3</sub> are the best chemical adsorbents. Although the chemical adsorbents have high adsorbent capacity and selectivity, but their regeneration is difficult.

At higher pressure (above 4 bar) activated carbons are more efficient than zeolites. The energy and cost of adsorption for activated carbons is nearly half of that of zeolites. On the other hand, zeolites (particularly 13X and 5A) have high selectivity for CO<sub>2</sub>, and they are suitable for application in the CO<sub>2</sub>/N<sub>2</sub> separation process. Generally, Zeolite 5A may have better adsorption efficiency at co-adsorbing SO<sub>2</sub>, NO and CO<sub>2</sub> than zeolite 13X. Using the pre-layer was suggested by researchers because of the presence of materials such as H<sub>2</sub>O, SO<sub>x</sub> and NO<sub>x</sub> in flue gas.

TABLE II  
COMPARISON BETWEEN SEVERAL ADSORPTION CYCLES FOR CO<sub>2</sub> CAPTURE  
PROCESS [20]

Process	CO <sub>2</sub> purity (%)	CO <sub>2</sub> recovery (%)
ESA	23.33	92.57
VPSA	99	53-70
PTSA	99	90
2-bed-2-step PSA	18	90
VPSA	99.5-99.8	34-69
PSA	99.5	69
PSA/VSA	58-63	70-75
VSA	90	90
PSA/VSA	58	87
PSA/VSA	82.7	17.4
3-bed VSA	90-95	60-70
TSA	95	81
ESA	89.7	79
PSA	16	89

In order to achieve more selective separation CO<sub>2</sub> from flue gas the modified adsorbent surface was considered. Furthermore, the most modified adsorbents are highly selective towards acid gases in mixtures including of nitrogen, oxygen, hydrogen and methane even at very low concentrations, and also the presence of moisture in the feed does not affect its performance. New adsorbents such as honeycomb monolith, MOFs, CHAs (NaCHA and CaCHA), PMO (MCM and SBA) and MSPs (Na<sub>2</sub>SiO<sub>4</sub>) are suitable adsorbents for selective CO<sub>2</sub> separation but they require more researches and studies.

It can be seen among the various adsorption cycle, the productivity and CO<sub>2</sub> recovery of VTSA, VSA and TSA are in order TSA < VSA < VTSA.

### ACKNOWLEDGEMENT

The authors gratefully acknowledge that they received financial support in the form of a research from the National Petrochemical Company (NPC), Iran.

### REFERENCES

- [1] Zangeneh, F.T., S. Sahebdehfar, and M.T. Ravanchi, "Conversion of carbon dioxide to valuable petrochemicals: An approach to clean development mechanism," *Journal of Natural Gas Chemistry*, **20**(3): p. 219-231. 2011.
- [2] Li, G., P. Xiao, P.A. Webley, J. Zhang, and R. Singh, "Competition of CO<sub>2</sub>/H<sub>2</sub>O in adsorption based CO<sub>2</sub> capture," *Energy Procedia*, **1**(1): p. 1123-1130. 2009.

TABLE III  
ADSORPTION CAPACITY OF DIFFERENT ADSORBENTS FOR POST-COMBUSTION CO<sub>2</sub> CAPTURE

Sorbent	Operating Temperature (°C)	Operating Pressure (kPa)	CO <sub>2</sub> Capture Capacity (mol CO <sub>2</sub> /kg sorbent)	Regeneration Cycles, n	CO <sub>2</sub> Capture Capacity Remained after n cycles (%)	Researchers	References
<b>Physical Adsorbents</b>							
AC (4%KOH)	30	30	0.55	-	-	Guo et al.[?]	[27]
AC (EDAA + EtOH <sup>b</sup> )	30	30	0.53	-	-	Guo et al.	[27]
AC (4%KOH + EDAA + EtOH <sup>b</sup> )	30	30	0.64	-	-	Guo et al.	[27]
MCM-41	25	100	0.62	-	-	Serna-Guerrero et al.	[27]
MCM-41(DEA <sup>c</sup> )	75	100	1.26	-	-	Franchi et al.	[27]
MCM-41 (50% PEI <sup>d</sup> )	75	100	2.52	-	-	Franchi et al.	[27]
Activated carbon (AC)	30	30	0.35	-	-	Guo et al.	[27]
MCM-41 (50% PEI <sup>d</sup> ) “molecular basket”	75	100	2.95	-	-	Guo et al.	[27]
PE <sup>e</sup> -MCM-41	25	100	0.50	-	-	Serna-Guerrero et al.	[27]
PE <sup>e</sup> -MCM-41(TRI <sup>f</sup> )	25	100	2.85	-	-	Serna-Guerrero et al.	[27]
PE-MCM-41(DEA <sup>c</sup> )	75	100	2.36	-	-	Franchi et al.	[27]
MCM-48	25	100	0.03	-	-	Jang et al.	[27]
MCM-48(APTS <sup>g</sup> )	25	100	0.64	-	-	Jang et al.	[27]
Lithium zirconate	400	100	5.00	-	-	Oliveira et al.	[27]
Lithium orthosilicate	600	100	6.13	-	-	Oliveira et al.	[27]
Calcium oxide	600	100	17.30	-	-	Oliveira et al.	[27]
Magnesium hydroxide	200	103	3.00	-	-	Siriwardane et al.	[27]
Magnesium oxide (mesoporous)	100	100	2.27	-	-	Bhagiyalakshmi et al.	[27]
Activated carbon	30	110	1.58	-	-	Mercedes et al.	[27]
MCM-41	25	100	0.62	-	-	Serna-Guerrero et al.	[27]
Molecular basket’ MCM-41(50%PEI)	75	100	2.50	8	96.0	Xu et al.	[27]
PE-MCM-41(TRI)	25	100	1.80	10	94.4	Serna et al.	[21]
PE-MCM-41(DEA)	25	100	2.90	7	96.6	Franchi et al.	[27]
MWNT	60	101	1.30	-	-	Hsu et al.	[18]
MWNT	60	101	1.70	-	-	Hsu et al.	[18]
<b>Chemical Adsorbents</b>							
Mesoporous (MgO)	25	101	1.80	3	100	Bhagiyalakshmi et al.	[27]
CaO nanopods	600	101	17.50	50	61.1	Yang et al.	[42]
CaO derived from nanosized CaCO <sub>3</sub>	650	101	16.70	100	22.2	Florin et al.	[27]
CaO–MgAl <sub>2</sub> O <sub>4</sub> (Spinel Nanoparticles)	650	101	9.10	65	84.6	Li et al.	[27]
Nano CaO/Al <sub>2</sub> O <sub>3</sub>	650	101	6.00	15	61.7	Wu et al.	[27]
Lithium silicate Nanoparticles	610	101	5.77	-	-	Ochoa-Fernández et al.	[27]
Nanocrystalline Li <sub>2</sub> ZrO <sub>3</sub> particles	575	101	6.10	8	100	Khomane et al.	[27]
CaO/Al <sub>2</sub> O <sub>3</sub>	650	101	6.02	-	-	Wu et al.	[27]
Lithium Silicate nano particles	600	101	5.00	-	-	Essaki et al.	[30]
HTI-HNa	300	134	1.11	50	93.3	Lee et al.	[27]

- [3] Thiruvenkatachari, R., S. Su, H. An, and X.X. Yu, "Post combustion CO<sub>2</sub> capture by carbon fibre monolithic adsorbents," *Progress in Energy and Combustion Science*. **35**(5): p. 438-455. 2009.
- [4] Dantas, T.L.P., F.M.T. Luna, I.J. Silva Jr, A.E.B. Torres, D.C.S. Azevedo, A.E. Rodrigues, and R.F.P.M. Moreira, "Carbon dioxide-nitrogen separation through pressure swing adsorption," *Chemical Engineering Journal*. **172**(2-3): p. 698-704. 2011.
- [5] Choi, S., J.H. Drese, and C.W. Jones, "Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources," *ChemSusChem*. **2**(9): p. 796-854. 2009.
- [6] Dechamps, P., *CO<sub>2</sub> Capture and Storage Projects*, E. 22574, Editor. 2007.
- [7] Maroto-Valer, M.M., Z. Tang, and Y. Zhang, "CO<sub>2</sub> capture by activated and impregnated anthracites," *Fuel Processing Technology*. **86**(14-15): p. 1487-1502. 2005.
- [8] Garnier, C., G. Finqueneisel, T. Zimny, Z. Pokryszka, S. Lafortune, P.D.C. Défossez, and E.C. Gaucher, "Selection of coals of different maturities for CO<sub>2</sub> Storage by modelling of CH<sub>4</sub> and CO<sub>2</sub> adsorption isotherms," *International Journal of Coal Geology*. **87**(2): p. 80-86. 2011.
- [9] Li, J.-R., Y. Ma, M.C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P.B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*. **255**(15-16): p. 1791-1823. 2011.
- [10] Plaza, M.G., S. García, F. Rubiera, J.J. Pis, and C. Pevida, "Post-combustion CO<sub>2</sub> capture with a commercial activated carbon: Comparison of different regeneration strategies," *Chemical Engineering Journal*. **163**(1-2): p. 41-47. 2010.
- [11] Damen, K., M.v. Troost, A. Faaij, and W. Turkenburg, "A comparison of electricity and hydrogen production systems with CO<sub>2</sub> capture and storage. Part A: Review and selection of promising conversion and capture technologies," *Progress in Energy and Combustion Science*. **32**(2): p. 215-246. 2006.
- [12] Grande, C.A., R.P.L. Ribeiro, E.L.G. Oliveira, and A.E. Rodrigues, "Electric swing adsorption as emerging CO<sub>2</sub> capture technique," *Energy Procedia*. **1**(1): p. 1219-1225. 2009.
- [13] Sahebdelfar, S., F. Tahriri Zangeneh, and M. Takht Ravanchi, *Chemical Recycling of Carbon Dioxide to Valuable Petrochemicals*, in *The 7th APCSEET conference*. 2009: Qingdao, China.
- [14] Takht Ravanchi, M., S. Sahebdelfar, and F. Tahriri Zangeneh, *Carbon Dioxide Sequestration in Petrochemical Industries with the Aim of Reduction in Greenhouse Gas Emissions*, in *The 7th APCSEET conference*. 2009: Qingdao, China. p. 173-178.
- [15] Wang, M., A. Lawal, P. Stephenson, J. Sidders, and C. Ramshaw, "Post-combustion CO<sub>2</sub> capture with chemical absorption: A state-of-the-art review," *Chemical Engineering Research and Design*. **89**(9): p. 1609-1624. 2011.
- [16] Pellerano, M., P. Pré, M. Kacem, and A. Delebarre, "CO<sub>2</sub> capture by adsorption on activated carbons using pressure modulation," *Energy Procedia*. **1**(1): p. 647-653. 2009.
- [17] Chaffee, A.L., G.P. Knowles, Z. Liang, J. Zhang, P. Xiao, and P.A. Webley, "CO<sub>2</sub> capture by adsorption: Materials and process development," *International Journal of Greenhouse Gas Control*. **1**(1): p. 11-18. 2007.
- [18] Chiao, C.-H., J.-L. Chen, C.-R. Lan, S. Chen, and H.-W. Hsu, "Development of carbon dioxide capture and storage technology - taiwan power company perspective," *Sustain. Environ. Res.* **21**(1): p. 1-8. 2011.
- [19] Feron, P.H.M., "Exploring the potential for improvement of the energy performance of coal fired power plants with post-combustion capture of carbon dioxide," *International Journal of Greenhouse Gas Control*. **4**(2): p. 152-160. 2010.
- [20] Clausse, M., J. Merel, and F. Meunier, "Numerical parametric study on CO<sub>2</sub> capture by indirect thermal swing adsorption," *International Journal of Greenhouse Gas Control*. **5**(5): p. 1206-1213. 2011.
- [21] Serna-Guerrero, R. and A. Sayari, "Modeling adsorption of CO<sub>2</sub> on amine-functionalized mesoporous silica. 2: Kinetics and breakthrough curves," *Chemical Engineering Journal*. **161**(1-2): p. 182-190. 2010.
- [22] Pevida, C., M.G. Plaza, B. Arias, J. Feroso, F. Rubiera, and J.J. Pis, "Surface modification of activated carbons for CO<sub>2</sub> capture," *Applied Surface Science*. **254**(22): p. 7165-7172. 2008.
- [23] Zhang, J., P. Xiao, G. Li, and P.A. Webley, "Effect of flue gas impurities on CO<sub>2</sub> capture performance from flue gas at coal-fired power stations by vacuum swing adsorption," *Energy Procedia*. **1**(1): p. 1115-1122. 2009.
- [24] Martunus, Z. Helwani, A.D. Wiheeb, J. Kim, and M.R. Othman, "Improved carbon dioxide capture using metal reinforced hydrotalcite under wet conditions," *International Journal of Greenhouse Gas Control*. **7**(0): p. 127-136. 2012.
- [25] Meng, L.-Y. and S.-J. Park, "Influence of MgO template on carbon dioxide adsorption of cation exchange resin-based nanoporous carbon," *Journal of Colloid and Interface Science*. **366**(1): p. 125-129. 2012.
- [26] Sevilla, M. and A.B. Fuertes, "CO<sub>2</sub> adsorption by activated templated carbons," *Journal of Colloid and Interface Science*. **366**(1): p. 147-154. 2012.
- [27] Lee, Z.H., K.T. Lee, S. Bhatia, and A.R. Mohamed, "Post-combustion carbon dioxide capture: Evolution towards utilization of nanomaterials," *Renewable and Sustainable Energy Reviews*. **16**(5): p. 2599-2609. 2012.
- [28] Herzog, H., J. Meldon, and A. Hatton, *Advanced Post-Combustion CO<sub>2</sub> Capture*. 2009.
- [29] Besson, R., M. Rocha Vargas, and L. Favergeon, "CO<sub>2</sub> adsorption on calcium oxide: An atomic-scale simulation study," *Surface Science*. **606**(3-4): p. 490-495. 2012.
- [30] Essaki, K., M. Kato, and K. Nakagawa, "CO<sub>2</sub> removal at high temperature using packed bed of lithium silicate pellets," *Journal of the Ceramic Society of Japan*. **114**:7: p. 39-42. 2006.
- [31] Anbia, M. and V. Hoseini, "Development of MWCNT@MIL-101 hybrid composite with enhanced adsorption capacity for carbon dioxide," *Chemical Engineering Journal*. **191**(0): p. 326-330. 2012.
- [32] Wang, J., L.A. Stevens, T.C. Drage, and J. Wood, "Preparation and CO<sub>2</sub> adsorption of amine modified Mg-Al LDH via exfoliation route," *Chemical Engineering Science*. **68**(1): p. 424-431. 2012.
- [33] Sakurovs, R., S. Day, and S. Weir, "Relationships between the sorption behaviour of methane, carbon dioxide, nitrogen and ethane on coals," *Fuel*. **97**(0): p. 725-729. 2012.
- [34] Weniger, P., J. Francú, P. Hemza, and B.M. Krooss, "Investigations on the methane and carbon dioxide sorption capacity of coals from the SW Upper Silesian Coal Basin, Czech Republic," *International Journal of Coal Geology*. **93**(0): p. 23-39. 2012.
- [35] Shafeeyan, M.S., W.M.A. Wan Daud, A. Houshmand, and A. Arami-Niya, "The application of response surface methodology to optimize the amination of activated carbon for the preparation of carbon dioxide adsorbents," *Fuel*. **94**(0): p. 465-472. 2012.
- [36] Plaza, M.G., C. Pevida, B. Arias, J. Feroso, F. Rubiera, and J.J. Pis, "A comparison of two methods for producing CO<sub>2</sub> capture adsorbents," *Energy Procedia*. **1**(1): p. 1107-1113. 2009.
- [37] Siriwardane, R.V., M.-S. Shen, E.P. Fisher, and J.A. Poston, "Adsorption of CO<sub>2</sub> on Molecular Sieves and Activated Carbon," *Energy & Fuels*. **15**(2): p. 279-284. 2001.
- [38] Vatalis, K.I., A. Laaksonen, G. Charalampides, and N.P. Benetis, "Intermediate technologies towards low-carbon economy. The Greek zeolite CCS outlook into the EU commitments," *Renewable and Sustainable Energy Reviews*. **16**(5): p. 3391-3400. 2012.
- [39] Cui, X., R.M. Bustin, and G. Dipple, "Selective transport of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in coals: insights from modeling of experimental gas adsorption data," *Fuel*. **83**(3): p. 293-303. 2004.
- [40] Jang, D.-I. and S.-J. Park, "Influence of nickel oxide on carbon dioxide adsorption behaviors of activated carbons," *Fuel*. **0**(0): 2012.
- [41] Abid, H.R., G.H. Pham, H.-M. Ang, M.O. Tade, and S. Wang, "Adsorption of CH<sub>4</sub> and CO<sub>2</sub> on Zr-metal organic frameworks," *Journal of Colloid and Interface Science*. **366**(1): p. 120-124. 2012.
- [42] Xiang, Z., Z. Hu, D. Cao, W. Yang, J. Lu, B. Han, and W. Wang, "Metal-Organic Frameworks with Incorporated Carbon Nanotubes: Improving Carbon Dioxide and Methane Storage Capacities by Lithium Doping," *Angewandte Chemie International Edition*. **50**(2): p. 491-494. 2011.
- [43] Liu, Z., C.A. Grande, P. Li, J. Yu, and A.E. Rodrigues, "Multi-bed Vacuum Pressure Swing Adsorption for carbon dioxide capture from flue gas," *Separation and Purification Technology*. **81**(3): p. 307-317. 2011.
- [44] Zhang, J., R. Singh, and P.A. Webley, "Alkali and alkaline-earth cation exchanged chabazite zeolites for adsorption based CO<sub>2</sub> capture," *Microporous and Mesoporous Materials*. **111**(1-3): p. 478-487. 2008.
- [45] Deng, H., H. Yi, X. Tang, Q. Yu, P. Ning, and L. Yang, "Adsorption equilibrium for sulfur dioxide, nitric oxide, carbon dioxide, nitrogen on 13X and 5A zeolites," *Chemical Engineering Journal*. **188**(0): p. 77-85. 2012.
- [46] Yang, R., G. Liu, M. Li, J. Zhang, and X. Hao, "Preparation and N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> adsorption of super activated carbon derived from biomass

- source hemp (*Cannabis sativa* L.) stem," *Microporous and Mesoporous Materials*. **158**(0): p. 108-116. 2012.
- [47] Alcañiz-Monge, J., D. Cazorla-Amorós, A. Linares-Solano, S. Yoshida, and A. Oya, "Effect of the activating gas on tensile strength and pore structure of pitch-based carbon fibres," *Carbon*. **32**(7): p. 1277-1283. 1994.
- [48] Gargiulo, N., F. Pepe, and D. Caputo, "Modeling carbon dioxide adsorption on polyethylenimine-functionalized TUD-1 mesoporous silica," *Journal of Colloid and Interface Science*. **367**(1): p. 348-354. 2012.
- [49] Millward, A.R. and O.M. Yaghi, "Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature," *Journal of the American Chemical Society*. **127**(51): p. 17998-17999. 2005.
- [50] Lin, L.-Y. and H. Bai, "Continuous generation of mesoporous silica particles via the use of sodium metasilicate precursor and their potential for CO<sub>2</sub> capture," *Microporous and Mesoporous Materials*. **136**(1–3): p. 25-32. 2010.
- [51] Mishra, A.K. and S. Ramaprabhu, "Palladium nanoparticles decorated graphite nanoplatelets for room temperature carbon dioxide adsorption," *Chemical Engineering Journal*. **187**(0): p. 10-15. 2012.
- [52] Aziz, B., N. Hedin, and Z. Bacsik, "Quantification of chemisorption and physisorption of carbon dioxide on porous silica modified by propylamines: Effect of amine density," *Microporous and Mesoporous Materials*. **159**(0): p. 42-49. 2012.
- [53] Chen, C., J. Kim, and W.-S. Ahn, "Efficient carbon dioxide capture over a nitrogen-rich carbon having a hierarchical micro-mesopore structure," *Fuel*. **95**(0): p. 360-364. 2012.