# Carbon Dioxide Sequestration: A Review on the Current Techniques and the Way Forward

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The effects of  $CO_2$  released from the combustion of fossil fuel and the ensuing global warming have caused a noticeable climate change throughout the world. The resulting efforts have been geared to reducing and removing atmospheric  $CO_2$ . One of the most prominent efforts undertaken by researchers worldwide is to capture and store  $CO_2$  or carbon dioxide capture and sequestration (CCS) using various methods and techniques. Post-combustion capture seems promising in terms of design, but more importantly, it can be easily integrated into existing plants thus providing a cheap and instant improvement. Activated carbon adsorption method seems to be the most cost efficient for post-combustion capture as its precursors are cheap and abundant, even though zeolite and ZIF counterparts show better selectivity and adsorption but are more expensive. In this paper, different ideas of CCS are reviewed individually and discussed with the sole aim of presenting the next step for achieving a sustainable method for the removal of atmospheric  $CO_2$ .

Key words: Post-combustion; CO<sub>2</sub> separation; CO<sub>2</sub> adsorption and removal

In recent years, there has been a growing environmental concern among researchers for global warming and climate changes. This has in turn driven research activities towards developing improved and efficient processes and technologies to reduce environmental impacts due to human activities. It is an established fact that global temperature has risen with measurable consistency to the increase in atmospheric CO<sub>2</sub>. In the mid 1960's, the global temperature rose by  $0.2^{\circ}$ C, and by the 1980's the global temperature has risen by  $0.4^{\circ}$ C [1]. It is predicted that if the upward trend continues, with the amount of CO<sub>2</sub> within that time period doubling, the global temperature will rise by  $3^{\circ}$ C with an error of  $\pm 1.5^{\circ}$ C [2].

One of the main contributors to global warming is the anthropogenic emissions of  $CO_2$  gas [3]. It has been reported that  $CO_2$  has the highest negative impact on the observed greenhouse effect, which causes up to approximately 55% of the global warming [4]. This is mainly attributed to  $CO_2$  causing greater adsorption of thermal radiation from the Earth's surface, and thus increases the overall air temperature within the troposphere [2].

From the Intergovernmental Panel on Climate Change (IPCC)'s fourth assessment report, the anthropogenic  $CO_2$  emission has shown a steady increase from 2005 up to recent years. Furthermore, global annual  $CO_2$  emissions due to fossil fuel use

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grew by 80% from 1970 to 2004 [5]. There are many factors that have direct or indirect influence in the level of CO<sub>2</sub> emission. Many studies have been done on  $CO_2$  emission and concluded that global  $CO_2$ emission is far from stabilizing, but instead is experiencing a significant increase. The factors contributing to this increase include economic development, population growth, technological advancement, transportation, lifestyle enhancement, and international trade [6]. Therefore, carbon capture technologies or methods which target large point sources of CO<sub>2</sub> emission should be looked into. These large point sources of CO<sub>2</sub> emission are the power and industrial sectors. For example, coal-based power plants, natural and synthetic gas processing plants, and cement plants are a few vital sectors which have been identified as main contributors of CO<sub>2</sub> emission. These sectors, when combined, currently dominate global CO<sub>2</sub> emission, which accounts for about 60% of total CO<sub>2</sub> emission [5].

#### 1. Carbon Capture and Sequestration (CCS)

With the continual increase of energy consumption, concerns over the increasing atmospheric concentration of anthropogenic greenhouse gases continue to grow as well. Therefore, the need for Carbon Capture and Sequestration (CCS) to combat the ever increasing effective  $CO_2$  emission is well justified.

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According to IPCC 2005, CCS is defined as a "process consisting of the separation of  $CO_2$  from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere" [7]. Therefore, from this definition, we have to consider the three basic stages of CCS, namely; separation of  $CO_2$  from the stream of the flue gas, transportation, and subsequently, long term storage.

Currently, there are three main approaches considered for  $CO_2$  capture for power plants, namely pre-combustion, post-combustion, and oxy-combustion [3]. The three main approaches were further explained by Kanniche and his team as the following [8]:

- 1. Pre-combustion capture: capture of CO<sub>2</sub> in a synthetic gas after conversion of CO into CO<sub>2</sub>;
- 2. Post-combustion capture: capture of CO<sub>2</sub> gas after the complete combustion of the fuel;
- 3. Capture in oxy-combustion: oxy-combustion is the process of fuel combustion using pure oxygen. This method of capture consists of the combustion in oxygen together with the recycling of exhaust gases and the purification of  $CO_2$  flow to eliminate the incondensable gases.

From these three approaches, post-combustion capture is considered to be the simplest in terms of implementation, and therefore the most viable and is the main topic of this review paper. This is because the separation and capture process can easily be integrated into the existing plant after the combustion phase [9]. On the other hand, other approaches may need alterations or modifications to the existing flow or layout of the plant and thereby increasing the cost factor. However, post-combustion capture is not without flaws. Unlike pre-combustion and oxycombustion capture, the stream to be treated in postcombustion capture is much more diluted in CO<sub>2</sub>. This does not only make the separation process more complex, but also increases the overall energy penalty due to the lowered flue gas pressure [10].

From the three basic stages of CCS mentioned, the first stage, which is the separation stage (i.e.  $CO_2$ capture), is the most energy intensive. This basically means that it will largely determine the overall cost (up to about 75–80% of the total cost) of the CCS process [11]. As such, this stage requires the most attention and consideration.

A large number of separation technologies for post-combustion  $CO_2$  capture have emerged, from the growing environmental concerns. In this review paper, five new emerging methods, namely: (a) adsorption; (b) physical absorption; (c) chemical absorption; (d) cryogenics separation; and (e) membranes are explored and explained [9, 10, 11].

# 2. Challenges of CO<sub>2</sub> Capture

Prior to discussing the potential  $CO_2$  capture materials and technologies, it is imperative to first identify the key challenges that many researchers are facing in the development of  $CO_2$  capture. There are many methods and approaches currently being explored and are in their respective development stages. However, they are still not ready for large scale implementations on the currently available power plants. This is due to the many reasons encountered. Some of the primary



Figure 1. CO<sub>2</sub> capture technologies and methods modified from: [10, 11]

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reasons include [3, 10]:

- 1. Lack of implementation or demonstration in a large scale
- 2. The required energy, both power and steam, of transportation and transfer to the carbon capture plant would reduce the output of the plant by approximately one-third
- 3. It would be simply not cost effective at the current process phase
- 4. Any chemical employed to capture CO<sub>2</sub> will be rapidly depleted, unless it is regenerable
- 5. Any particular chemical utilizing CO<sub>2</sub> as a reactant will rapidly saturate the global market for that particular chemical

#### 3. Conventional CO<sub>2</sub> Capture

Separation of carbon dioxide,  $CO_2$  from natural gas and hydrogen via amine scrubbing has been utilized since the 1930's [12]. Then, this technology was tested and used on a larger scale for  $CO_2$  capture from coalfired power plants. Since then, post-combustion "wetscrubbing"  $CO_2$  capture technologies have been employed industrially for the past 50 years, which are predominantly based on the primary alkanolamine, monoethylamine (MEA) [10]. Post-combustion absorption by means of MEA has since been used as the reference technology to separate  $CO_2$  from flue gases due to the high selectivity of amines towards CO<sub>2</sub> and is currently the most developed technology employed in the industry [9].

Figure 2 shows the basic system layout of postcombustion absorption by amine scrubbing used in the 1930s. Modern systems found in power plants nowadays are based on this system, which also consists of two main elements: an absorber where  $CO_2$ is removed and a regenerator (or stripper) where  $CO_2$ is released in a concentrated form and the original solvent is recovered. However, some of the solvent is unrecoverable and may be lost during the process due to physical losses, entrainment, vaporization and/or chemical degradation. To regenerate the solvent, a large amount of heat is required. This heat is usually drawn from the steam cycle, which significantly reduces the overall efficiency of the power plant [9].

The overall amine scrubbing process is as follows: firstly, the aqueous amine solution is allowed to flow down from the top of an absorption tower. A gaseous stream of flue gas containing CO<sub>2</sub> is introduced at the bottom. The gas is pump through the absorber by a blower. At a temperature of about  $400^{\circ}$ C, the reaction of CO<sub>2</sub> with the amine follows the zwitterion mechanism route to produce carbamates. Then, the liquid CO<sub>2</sub>-rich amine solvent is passed from the absorber column to a stripping tower. In the stripping tower, the mixture is heated with steam to release CO<sub>2</sub>. The subsequent regeneration process of the chemical solvent is carried out at high temperature and increased pressure, a little higher than atmospheric pressure. However, this high heat of formation related with carbamate production causes great energy penalty for regeneration of the solvent.



Figure 2. The amine scrubbing process utilized by Bottoms in 1930 (adapted from [12])

Finally, after the regeneration step, the amine solution is cycled back to the absorption tower for further  $CO_2$  absorption [10, 13].

From the system and process explained above, it can clearly be seen that the amine scrubbing for postcombustion capture can be easily retrofitted to existing power plants and industries in suitable locations. The use of MEA is also suitable for low  $CO_2$  partial pressure flue gas. Furthermore, increasing MEA concentration has been proved to decrease the thermal energy requirement. However, when increasing MEA concentration, corrosion problems have to be taken into account [9].

Despite the popularity of amine scrubbing for post-combustion capture, many researches showed that it is still heavily flawed. Veawab et al. [14] did a study on solvent formulation for CO<sub>2</sub> capture from flue gas and highlighted some of the disadvantages of the most common amine scrubbing solvent, MEA. In the study, some of the practical problems faced included high rate of energy consumption required for solvent regeneration, corrosion of the process equipment, high solvent losses, and also high rate of degradation. The corrosion problem was further explored by Kittel et al. [15]. In an industrial process, corrosion is one of the major operational problems faced. It was reported in Kittel's study that MEA caused this problem to escalate. This is due to the corrosive nature of MEA, which is a primary amine. Furthermore, one of the components of flue gas, oxygen reacts with the amine to form corrosive degradation products [15]. In a recent research [16], Fytianos and his team of researchers further supported this by identifying each specific component that contributes to corrosion. In Fytianos's research, four of MEA degradation products (HeGly, HEEDA, Bicine and BHEOX) have been identified to contribute to the increase in corrosivity [16]. Furthermore, the two fluid phases used in this system are highly interdependent on each other, presenting operational limitations and may also produce emulsions, foaming, unloading, and flooding [9].

# 4. Post-combustion Routes/Technologies

From Figure 1, four main technologies are currently being developed for post-combustion carbon capture, namely adsorption, absorption, cryogenics, and membrane technology. A brief introduction of each technology will be discussed to provide sufficient background for this review paper.

# 4.1 Adsorption

Adsorption is a physical process that involves the interactivity between the sorbent and target molecules, which in this case are  $CO_2$  molecules. The target  $CO_2$ 

molecules are attracted and trapped by surface groups of the sorbent also known as physi-sorption [13]. One of the advantages of the adsorption method is the regenerative capabilities of the adsorbent. The adsorbent can be regenerated via two methods: the application of heat (temperature swing adsorption, TSA) or the reduction of pressure (pressure swing adsorption, PSA).

When determining an appropriate CO<sub>2</sub> capture adsorbent, the following components should be considered; low-cost raw materials, low heat capacity, fast kinetics, high CO2 adsorption capacity, high CO2 selectivity, and thermal, chemical, and mechanical stabilities under extensive cycling [17]. Potential solid physical adsorbents that have been considered for CO<sub>2</sub> capture applications include microporous and mesoporous materials (carbon-based sorbents such as activated carbon and carbon molecular sieves, zeolites, and chemically modified mesoporous materials), metal oxides, hydrotalcite-like compounds, and many others [10].

However, current adsorption systems may not yet be suitable for large-scale applications. This is mainly due to the low adsorption capacity of most currently available adsorbents. In addition, the targeted flue gas streams must reach certain  $CO_2$ concentration levels as most available adsorbents generally have low selectivity [18]. In this review paper, physical adsorption by means of activated carbon and mesoporous zeolites are emphasized and reviewed.

# 4.1.1 Activated Carbon

Carbonaceous adsorbents such as activated carbon (AC) have been extensively studied for CO<sub>2</sub> capture. ACs are carbons with high microporosity with both high internal surface area and porosity. Commercially, AC is one of the most common adsorbents used for the removal of organic compounds from both air and water sources. This is because the raw materials required to produce AC are cheap and abundant. Agricultural by-products have been widely used as the raw material due to its high carbon content, low inorganics, and availability at low prices, or sometimes freely available as it is considered as waste material. For example, oil palm shells, guava seeds, and papaya seeds [19, 20, 21, 22]. Furthermore, it can produce AC with good adsorption capacity, considerable mechanical strength, and low ash content [23].

Table 1 summarizes the studies by researchers to prepare ACs from agricultural by-products using various methods. Table 2 shows ACs prepared from agricultural by-products for carbon capture.

Raw material	Activation method	Reference
Papaya seeds	Physical Activation	[19]
Oil palm shells	Physical/chemical Activation	[20, 22]
Guava seeds	Physical Activation	[21]
Marigold straw (TageteserectaL)	Chemical Activation	[24]
Argan shells	Physical Activation with steam	[25]
Coconut shells	Physical Activation	[26]
Aguaje (Mauritiaflexuosa)	Chemical Activation via Phosphorus Acid	[27]
Olive fruit stones ( <i>Oleaeuropaea</i> L.)	Chemical Activation via Phosphorus Acid	[27]
Cherry stones	Chemical and Physical Activation	[28]
Eucalyptus wood	Chemical Activation via Phosphoric Acid	[29]
Reedy grass leaves	Chemical Activation via Phosphoric Acid	[30]
Pine nut shell	Chemical Activation via KOH	[31]
Wheat straw	Pyrolysis	[32]
Corn straw	Pyrolysis	[32]
Sunflower seed shells	Pyrolysis/Gasification	[33]
Pine cones	Pyrolysis/Gasification	[33]
Rapeseed	Pyrolysis/Gasification	[33]
Cotton refuse	Pyrolysis/Gasification	[33]
Olive refuse	Pyrolysis/Gasification	[33]
Pinus radiate	Physical Activation	[34]
Eucalyptus maculate	Physical Activation	[34]
Sugar cane bagasse	Physical Activation	[34]

#### Table 1. Activated carbons prepared from agricultural by-products

When discussing the application of AC for carbon capture, two drawbacks can be observed. Firstly, its application is limited to treat high pressure gases as compared to low pressure flue gas capture [17]. Unfortunately, most, if not all target points for post-combustion carbon captures are low pressure and low CO2 concentration flue gases. The second drawback of using AC as an adsorbent is that it does not have sufficient selectivity towards CO2 separation from flue gases. AC utilizes its pore size to capture the target molecules, which in this case are large CO<sub>2</sub> molecules [13]. However, smaller gases compete with CO<sub>2</sub> molecules to penetrate and occupy the limited pores available on AC. N<sub>2</sub> is the most common gas which occupies pore spaces in the adsorbent. Other common gases found in flue gases which may compete for pore spaces include H<sub>2</sub>O, SO<sub>x</sub>, and NO<sub>x</sub>.

This causes the overall capture process to be less efficient as a lower degree of  $CO_2$  separation is achieved in each cycle [13].

In general, the low efficiency of AC for carbon capture in flue gases and its weak selectivity towards  $CO_2$  is not suitable for post-combustion applications. Despite these drawbacks, physical adsorption may still provide great contributions towards building a hybrid system. Currently, extensive research is being carried out to find more suitable raw materials for preparing AC in hopes of producing more selective adsorbents, adsorbents with higher capacities, better operating conditions, and more efficient packing structures [13]. If these goals can be achieved, it will be no doubt that adsorption via AC can be made a viable method for separating  $CO_2$  in the future.

Raw material	Activation method	AC preparation parameters	CO <sub>2</sub> capture/detection method	CO2 uptake capacity	Ref
Coconut shells	Commercial AC with NaOH impregnation	NaOH concentration of 24-48% Dwelling time of 1-4 hrs at room temperature	Fixed-bed column method CO <sub>2</sub> conc. was measured using an online	27.10 mg/g	[35]
			$CO_2$ analyzer (Quentek instrument, USA)		
Mango seed shells	Chemical activation with H <sub>3</sub> PO <sub>4</sub>	Raw sample was soak in H <sub>3</sub> PO <sub>4</sub> for 24 hrs at 110°C followed by thermal treatment at 400°C	Single column adsorption breakthrough measurement system	4.8 mmol g <sup>-1</sup>	[36]
			CO <sub>2</sub> conc. was measured using online Gas Chromatograph (GC7610, Chemito)		
Oil palm shells	Chemical activation with KOH and microwave irradiation	Raw sample was soaked in KOH for 2 hrs at 85°C and boiled until dry. Sample was kept in oven to completely remove moisture. Impregnated sample is then placed in a quartz reactor for microwave irradiation.	CO <sub>2</sub> adsorption capabilities were measured using a semi-automatic adsorption apparatus (NOVA-1200, Quantachrome)	Not specified	[37]
Eucalyptus	Chemical activation with	Impregnated with $H_3PO_4$ with a ratio of 2 g/g	Volumetric method which consists of two	3.22 mmol/g	[29]
wood	H <sub>3</sub> PO <sub>4</sub>	with a carbonization temperature of 450°C	high-pressure stainless steel vessels		[_,]
			Prior to adsorption test, helium was used		
			to determine the volume of AC. $CO_2$ adsorption was carried out at pressures		
			from 0 to 16 bar. Subsequently, by using		
			the SRK equation of state in MATLAB		
			adsorbed was calculated		
White wood	Physical activation with steam	Steam activation: Sample was loaded into a reactor and heated to 700°C with flowing nitrogen. Then steam was injected into the	Isothermal fixed-bed tubular reactor CO <sub>2</sub> adsorption capabilities were	AC steam : 59 $mg_{CO2}/g_{AC}$ AC CO <sub>2</sub> : 63	[38]
	Physical activation with CO <sub>2</sub>	reactor with a steam to carbon mass ratio of	measured using a micro-gas	$mg_{CO2}/g_{AC}$	
	Chemical activation with KOH		GC, Varian Inc, Walnut Creek, CA, USA)	mg <sub>CO2</sub> /g <sub>AC</sub>	

# **Table 2.** Performance of ACs prepared from agricultural by-products for carbon capture

		<ul> <li>CO<sub>2</sub> activation: Sample was placed in a fixed bed reactor with argon flow and temperature was raised to 890°C. The, argon gas was replaced with CO<sub>2</sub> gas for 100 min.</li> <li>Chemical activation: Sample was impregnated with KOH with a mass ratio of carbon to KOH of 0.81 for 4 hrs. Carbonization of the impregnated sample was carried out in a reactor with N<sub>2</sub> flow at 300°C for 1 hr then at 775°C for 2 hrs.</li> </ul>	equipped with a thermal conductivity detector (TCD)		
Biomass (gelatin & starch)	Dry chemical activation	Carbonization of the biomass pristine gelatin and starch and physical mixing at different ratios using electrical tubular furnace at 450°C. Then, the sample obtained was mixed with chemical activator such as KOH at fixed ratios, and heated in a tubular furnace at 700°C under inert atmosphere.	Volumetric method using Micromeritics ASAP 2020-surfacearea and porosity analyzer	7.49 mmol g <sup>-1</sup>	[39]
Corn straw	Physical and Chemical activation	Physical activation: Pyrolysis at 800°C with N <sub>2</sub> for inert conditions and CO <sub>2</sub> as activation gas. The activation time ranges from 20-60 min. Chemical activation: Samples (AC) prepared from physical activation were further activated by using KOH, HNO <sub>3</sub> and CH <sub>3</sub> COOH. The AC was mixed with acid solutions of different concentrations at room temperature for 48 hrs and at 100°C for 1hr.	Thermogravimetric analysis (TGA) method was used to determine the $CO_2$ adsorption properties, based on the weight of $CO_2$ adsorbed.	7.33 wt %	[40]
Stones of Yellow Mombin	Physical activation with CO <sub>2</sub> Chemical activation with KOH Chemical activation with H <sub>3</sub> PO <sub>4</sub> Chemical activation with HNO <sub>3</sub>	Physical activation: The raw samples were directly pyrolyzed at 500°C for 2 hrs under N <sub>2</sub> flow. The carbonized samples underwent gasification by CO <sub>2</sub> at 500°C for 2 hrs Chemical activation: KOH: Raw samples were mixed with 85% KOH solution at a 1:1 mass ratio, and refluxed 85°C for 4 hrs	Thermogravimetric studies (TGA) using the DTG-60HShimadzu equipment was used to determine the $CO_2$ adsorption properties, based on the weight of $CO_2$ adsorbed.	$\begin{array}{c} AC \ CO_2: 4.5 \ \% \ CO_2 \\ g^{-1} \\ AC \ KOH: \ 6.3 \ \% \\ CO_2 \ g^{-1} \\ AC \ H_3PO_4: \ 2.3 \ \% \\ CO_2 \ g^{-1} \\ AC \ HNO_3: \ 3.4 \ \% \\ CO_2 \ g^{-1} \end{array}$	[41]

		$H_3PO_4$ : Raw sample was refluxed with 10% $H_3PO_4$ at a mass ratio of 1:5 for 4hrs. Then the sample was pyrolyzed under $N_2$ flow at 500°C for 2 hrs			
		HNO <sub>3</sub> : Raw sample was refluxed with 10% HNO <sub>3</sub> at a mass ratio of 1:5 for 4 hrs. Then the sample was pyrolyzed under $N_2$ flow at 500°C for 2 hrs			
Palm shells	Steam activation and impregnation with MEA and DEA	Commercial AC produced from steam activation of palm shells was used. Impregnation of method: The AC was immersed in 3% w/v of MEA or DEA in methanol at room temperature for 15 min. Then it was placed in a water bath at 70°C for slow	Volumetric method which consisted of a loading cell and an adsorption cell.	4.2 mol kg <sup>-1</sup>	[42]

# 4.1.2 Zeolites

Another important physical adsorbent for carbon capture that has been widely reported are zeolites, which basically are microporous, crystalline aluminosilicates. These aluminosilicate-based materials represent a large segment of the global economy with the estimated revenue of up to \$350 billion annually [43, 44]. They have uniform pore structures and channel diameter range of 0.3 to 1.0 nm [45]. The zeolite framework is made from interlinked tetrahedral of silica, SiO<sub>4</sub> and alumina, AlO<sub>4</sub> joined together in various regular arrangements via shared oxygen atoms to form open crystal lattice containing cavities of molecular dimensions into which molecules can penetrate [46]. Due to the molecularsized cavities and pores in the zeolite matrix, it serves as a good shape-selective material for a wide range of separation applications. This shape selective ability of zeolites makes it exceptionally efficient for CO<sub>2</sub> separation.

Table 3 shows some of the zeolites and zeolite-like materials studied for their  $CO_2$  adsorption capabilities.

A large number of studies have been done on zeolites using different configurations to utilize and optimize its recycling capabilities as shown in Table 3. These different configurations include temperature swing and pressure swing adsorption. Moreover, when considering  $CO_2$  adsorption kinetics, zeolites are one of the fastest adsorbents to reach its equilibrium capacity. Zeolites can generally operate with high efficiency, given that the condition of the feed stream is completely dry. While low silica materials show high adsorption capacity and selectivity at low pressure with favorable isotherms, the presence of water strongly inhibits its  $CO_2$  adsorption capabilities [46].

In recent years, many researchers have attempted new novel zeolite composites to overcome its flaws and increase the  $CO_2$  capacity uptake. Many researchers have synthesized hybrid adsorbents by incorporating zeolites with amines in hopes to

overcome its flaws and increase CO2 capture efficiency. Jadhav et al. [51] synthesized a MEA zeolite 13X hybrid by impregnation of monoethanol amine (MEA) onto zeolite 13X. Furthermore, Jadhav et al. investigated the effects of temperature on the capture of CO<sub>2</sub> of this hybrid material [51]. Xu et al. [52] synthesized a MEA-modified  $\beta$ -zeolite and focused on its selectivity [52]. Su et al. [53] also synthesized a zeolite Y, which was modified using tetraethylenepentamine via impregnation method [53]. Chen et al. [54] attempted a zeolitepolyethylenimine hybrid by impregnation of polyethylenimine into zeolite 13X [54]. All of the hybrid zeolite compounds above have shown better CO<sub>2</sub> uptakes at elevated temperatures and better adsorption under wet conditions compared to native zeolites, which are requirements for post-combustion CO<sub>2</sub> capture [51, 52, 53, 54].

Liu *et al.* [55] aimed to solve the problem of selective  $CO_2$  capture under humid conditions by fabricating a shell around the zeolites. This will effectively hinder the diffusion of water molecules into the zeolite core. Liu and his team of researchers chose to fabricate the shell using a mesoporous silica-supported-amine via a sol-gel coating process. This novel adsorbent demonstrated good efficiency of  $CO_2$  capture, with an uptake of 5.05 mmol/g of  $CO_2$  [55].

Other novel composites of zeolites have been explored by different researchers. Chen *et al.* [56] synthesized a Pebax<sup>®</sup>/zeolite Y composite specifically for capture of CO<sub>2</sub> in flue gases. This composite consists of three layers, which are the inorganic zeolite Y, Pebax<sup>®</sup> layer, and the polydimethylsiloxane (PDMS) cover layer. It was reported by Chen *et* al. that this new Pebax<sup>®</sup>/zeolite Y composite showed a better CO<sub>2</sub>/N<sub>2</sub> selectivity. Chen *et al.* explained that the hydrophilic zeolite Y layer increased the adhesion between the Pebax<sup>®</sup> polymer layer and the substrate. This enables the preparation of a thinner and defectfree membrane. Furthermore, this composite has shown a lower mass transfer resistance of CO<sub>2</sub> molecules through the membrane [56].

Zeolites used	Adsorption capacities (mol kg <sup>-1</sup> )	References
Zeolite 13X (Room Temperature, 25°C)	2.8 - 3.9	[47]
Zeolite 13X (Elevated Temperature, 50°C)	1.43 - 2.49	[47]
Y and X Zeolites	3.1 - 4.6	[48]
LiY and NaY	0.45 - 1.17	[49]
Faujasite Y (CsY)	0.86 – 1.2	[50]
Faujasite Y (KY)	0.75 - 1.6	[50]

Table 3. Zeolites and zeolite-like materials studied for their CO<sub>2</sub> adsorption capabilities

MOF	Surface area (m²/g)	CO <sub>2</sub> capture capacity (wt %)	Adsorption pressure/temperature (bar/°C)	Ref
MOF-177	4508	60.0	35/25	[59]
MOF-200	4530	70.9	35/25	[59]
MOF-205	4460	59.9	35/25	[59]
MOF-210	6240	70.6	35/25	[59]
MOF-2	345	12.3	35/25	[60]
MOF-505	1547	31.0	35/25	[60]
Zn-MOF-74	816	32.4	35/25	[60]
HKUST-1	1781	32.0	35/25	[60]
IRMOF-11	2096	39.3	35/25	[60]
IRMOF-3	2160	45.1	35/25	[60]
IRMOF-6	2516	46.2	35/25	[60]
IRMOF-1	2833	48.8	35/25	[60]
Mg-MOF-74	1800	35.2	1/25	[61]

Table 4. CO<sub>2</sub> capture capacity in selected MOFs

#### 4.1.3 Metal-Organic Frameworks (MOFs)

Metal-Organic Frameworks (MOFs) are hybrid materials built from the coordination of organic ligands and metal ions or metal-containing clusters [57]. When discussing  $CO_2$  capture by adsorption, the main attribute that determines the adsorption capacity is the surface area of the adsorbent. The robust 3D structures and well defined crystallography give MOFs superior surface area compared to many other adsorbents [58]. For this purpose, many studies and research have been done on the  $CO_2$  capture capability of MOFs. Some of the notable studies are listed in Table 4.

While many research have been done on the capture capabilities of MOFs, many critical aspects of MOFs for  $CO_2$  capture have yet to be studied. In a review by Liu and his colleagues, Liu stated that many issues have been overlooked and MOFs are not yet ready for practical use. Some of these issues include: mechanical stability, volumetric capacity, heat conductivity, and  $CO_2$  transfer within MOFs [58].

# 4.1.4 Zeolitic Imidazolate Frameworks (ZIFs)

Zeolitic Imidazolate Frameworks (ZIFs) are a subclass of Metal-Organic Frameworks (MOFs) with tetrahedral networks that resemble those of zeolites. However, it is different from zeolites by the incorporation of with transition metals (Co, Cu, Zn, etc.) linked by imidazolate ( $C_3N_2H_3^- = Im$ ) ligands [62, 63]. The bridging angles of M-Im-M fragment in ZIFs have the same bridging angle as the preferred Si-O-Si angle (145°) in zeolites. This makes it possible to make new ZIFs with topologies based on those of

tetrahedral zeolites. Based on this knowledge, more than 90 types of ZIF structures have been reported [44]. Furthermore, ZIFs have good chemical and thermal stability, making it highly potential for applications such as gas adsorption, molecular separation [64, 65], and catalysis [66, 67]. Therefore, many researchers have narrowed their scope and focus on specific ZIFs to determine its  $CO_2$  capabilities.

ZIF-20 carbon capture properties were studied by Hayashi *et al.* [68]. He examined the gas separation properties of ZIF-20 by passing a mixture of CO<sub>2</sub>/CH<sub>4</sub> gas through a stainless steel column reactor. From his study, he was able to show that ZIF-20 has a gas uptake of up to 200 cm<sup>3</sup> g<sup>-1</sup> [68].

Banerjee *et al.* [69] came to a conclusion that ZIF-69 not only have high porosity, but also high selectivity towards CO<sub>2</sub>. From Banerjee's experiment of carbon capture using CO<sub>2</sub>/CO mixtures, it was observed that 1 liter of ZIF-69 can hold about 83 liters of CO<sub>2</sub> at 0°C and 1 atm [69].

Wang *et al.* [70] studied both ZIF-95 and ZIF-100 and also made comparisons on their CO<sub>2</sub> capture properties. Both ZIF-95 and ZIF-100 have great potentials in CO<sub>2</sub> capture owing to their huge cavities and constricted windows. This was further proven in Wang's study whereby he measured the adsorption of CO<sub>2</sub>, CH<sub>4</sub>, CO, and N<sub>2</sub>. The results showed a disproportionately higher affinity and capacity for CO<sub>2</sub> [70].

In general, zeolites, MOFs and ZIFs show great potential in flue gas CO<sub>2</sub> capture due to their favorable adsorption isotherms. However, due to its sensitivity to the presence of water, flue gas needs to be extensively dried before sending it to the adsorption feed stream [46]. Currently, new studies have emerged to look into the abilities of zeolites to modify their properties by impregnating or tethering active groups such as alkyl-amines onto their internal surfaces. By employing this strategy, its gas sorption properties for low pressure carbon capture can be improved [10].

# 4.1.5 Activated Carbon Grafted MOF

As discussed above, activated carbon has great potential for  $CO_2$  capture, if the low selectivity drawback can be addressed properly. Recently, a new idea has been tested, whereby activated carbon was combined with other materials to increase its capabilities. These hybrid adsorbents, however, are not yet fully explored. Many other potential precursors and methods have yet to be discovered. Several attempts, methods, and their efficiencies are discussed below.

Vidic & Siler [71] prepared activated carbons impregnated with chloride and chelating agents for vapor-phase mercury adsorption. A commercial activated carbon was impregnated with chloride, aminoanthraquinone, 2-(Aminomethyl)pyridine (picolyl amine), and thiol. The chloride-impregnated activated carbon showed great dynamic adsorption capacities. Both the aminoanthraquinone-impregnated and thiol-impregnated activated carbons also showed improved dynamic adsorption capacities compared to that of the commercial activated carbon [71].

Almasoudi & Mokoya, [72] attempted and successfully prepared activated ZIF- templated carbon via chemical vapor deposition (CVD) route, as a novel hydrogen storage method. A commercial ZIF was used in the experiment and was impregnated with furfuryl alcohol (FA), followed by polymerization, carbonization, and activation. Since carbon was activated in a confined space, within the ZIF, the resultant pores were much finer. It was reported that the new adsorbent synthesized was highly microporous with a surface area of  $3200 \text{ m}^2/\text{g}$  and pore volume of  $1.94 \text{ cm}^3/\text{g}$  [72]. A follow-up to these findings was made, whereby the same adsorbent was investigated for other applications and a more optimum preparation and impregnation methods [72, 73].

#### 4.2 Absorption

When discussing carbon capture by means of absorption, two approaches can be taken into account, namely, chemical absorption and physical absorption. In physical absorption for carbon capture, Henry's law is of concern whereby  $CO_2$  is absorbed into a solvent. Typical solvents used for physical absorption are Selexol (dimethyl ethers of polyethylene glycol) and Rectisol (methanol). This absorption process, however, requires high  $CO_2$  partial pressures. Therefore, energy consumption for the flue gas pressurization process needs to be considered [74].

On the other hand, chemical absorption utilizes the reaction of  $CO_2$  with a chemical solvent that forms weakly bonded intermediate compounds. This process may then be regenerated with the application of heat, producing the original solvent and  $CO_2$  stream [5]. Carbon separation by means of chemical absorption has a relatively high selectivity. Furthermore, a relatively pure  $CO_2$  stream could be produced by this method. Due to these factors, chemical absorption is currently applied for  $CO_2$  capture in industrial flue gases [11].

#### 4.2.1 Selexol and Rectisol

Both solvents used for Selexol and Rectisol, which are DPEG and MeOH, respectively, are noncorrosive and relatively non-toxic. To determine whether Selexol or Rectisol, or any other physical absorption process, is suitable, the process objectives and solvent characteristics have to be determined beforehand. The characteristics include selectivity of CO<sub>2</sub>, H<sub>2</sub>S, HCN, etc., effect of water content in the feed stream, concurrent hydrocarbon absorption with acid gas removal, solvent cost, solvent availability, cost efficiency, and thermal stability [75]. Table 5 compares some of the selected properties of Selexol and Rectisol.

Process/Solvent	Selexol (DPEG)	Rectisol (MeOH)	
Molecular weight	280	32	
Viscosity at 25°C (cP)	5.8	0.6	
Vapor pressure at 25°C (mmHg)	0.00073	125	
Boiling point at 760 mmHg (°C)	275	65	
Freezing point (°C)	-28	-92	
Maximum operating temperature (°C)	175	-	
Specific heat at 25°C	0.490	0.566	
CO <sub>2</sub> solubility at 25°C	0.485	0.425	

Table 5. Properties of Selexol and Rectisol adapted from: Burr & Lyddon [75]

The earliest use of Selexol, developed by Allied Signal to sweeten natural gas, bulk CO<sub>2</sub> removal and H<sub>2</sub>S removal, can be traced back to 1969 [76]. The Selexol process uses the Union Carbide Selexol solvent, which is a physical solvent that consists of DPEG (Dimethyl ether polyethylene glycol). The Selexol absorption process requires low temperature of  $0 - 5^{\circ}$ C. One advantage of the Selexol process is the capability of desorption from the rich Selexol solvent. This desorption can be accomplished by means of lowering the pressure or by stripping with air, inert gas or steam. Other than CO<sub>2</sub>, the solvent can be altered to selectively or simultaneously remove sulphur compounds, carbon dioxide, water, and also aromatic compounds. However, dehydration of the feed gas is required before using the Selexol process [77].

The advantages of using the Selexol process include [77]:

- 1. The temperature increase of the solvent in the absorber is not significant as there is no heat of chemical reaction.
- 2. Minimal cost for initial plant and operating procedures.
- 3. Regeneration of the solvent is by air stripping; it requires no re-boiler's heat.
- 4. Selexol process allows for construction of mostly carbon steel due to its non-aqueous and inert chemical characteristics.
- 5. The process could be operated at low pressure.

However, Selexol has its disadvantages. Selexol solvents have higher affinity towards heavy hydrocarbons, which will be removed with CO<sub>2</sub>. This essentially results in hydrocarbon losses. Although the process could be operated at lower pressure, higher operating pressure has been proved to increase efficiency [77].

The other absorption process discussed in this review paper is Rectisol. Commercially, Rectisol has been mainly used to treat synthetic gas, hydrogen and town gas streams, and also removes most impurities. The Rectisol process utilizes chilled methanol as a solvent. This is due to the high vapor pressure of methanol. Therefore, the process is normally operated at temperatures ranging from -2°C to 212°C; much lower than the Selexol process [78]. Like the Selexol process, different configurations can be used for the Rectisol process depending on the requirements and scale to optimize efficiency. Currently, the Rectisol process is mainly used for CO<sub>2</sub> removal in the natural gas industry [77].

The advantages of using the Rectisol process include [77]:

- 1. The Rectisol solvent, which consists of methanol, does not foam and is completely miscible with water. These properties help reduce losses.
- 2. It has good thermal and chemical stability.
- 3. It is non-corrosive.
- 4. No significant degradation problems are detected so far.
- 5. Carbon steel can be widely used for the equipment.
- 6. The rich solvent can be easily regenerated by flashing at low pressure, therefore eliminates the need for re-boiler's heat.

Rectisol does have some drawbacks as chilled methanol solvent may absorb metallic trace components such as mercury (Hg). This results in the formation of amalgams at low temperatures during the absorption process. Finally, employing Rectisol in this application requires a complex scheme, coupled with the need to refrigerate the solvent results in high capital and operating cost for the plant [77].

Some comparison studies between Selexol and Rectisol were conducted recently to determine the efficiency and comparisons between the two solvents. Chen and his team [74] studied the CO<sub>2</sub> capture capabilities of Selexol, Rectisol, and water at different parameters. It was found that at higher temperature, all solvents showed decrease in efficiency. Rectisol was found to have a higher absorption capacity, however, both Selexol and Rectisol were comparable [74]. Another research done by Strube and Manfrida [79] focused on the effectiveness of Selexol CO2 capture in different configurations. It was found that a configuration whereby two components, CO2 and H<sub>2</sub>S, were both captured simultaneously, the capture was less effective compared to a configuration with only one component to be captured [79].

#### 4.2.2 Ionic Liquid

Ionic liquids (ILs) are organic salts that exist in the liquid state at low temperatures (less than  $100^{\circ}$ C). Currently, ILs are studied for their potential as new non-volatile and reversible CO<sub>2</sub> absorbents for CO<sub>2</sub> separation. The main reason for ILs being chosen is due to their high CO<sub>2</sub> solubility [80]. Coulombic interaction between the ions of ILs causes no measurable vapor pressure up to their thermal decomposition point, which is usually greater than 300°C. Because of this absence of vapor pressure, these materials are highly attractive for gas processing. As stated by Bates *et al.*, ILs may be

thought of as "liquid solids", possessing both useful physical properties of both phases [81]. Therefore, ILs have been highlighted as a potential alternative for carbon capture.

In recent developments for IL CO<sub>2</sub> capture, supported liquid membranes using ionic liquids have been developed. Supported ionic liquid membranes (SILM) was studied by Zarca *et al.* [82] to separate carbon monoxide/hydrogen generated in certain industrial processes which involved hydrocarbon combustion. The result of this study has shown that SILM holds an advantage over polymeric membranes in terms of recovery and separation of carbon/hydrogen from N<sub>2</sub> rich gas streams [82].

Furthermore, other studies have shown that  $CO_2$  solubility and selectivity can be altered in response to the cation, anion, and substituents of the ionic liquids. One example of such phenomenon can be seen from the study made by Scovazzo *et al.* [83], whereby they explored the  $CO_2$  solubility of five different room-temperature ionic liquids (RTIL) [83].

In a study by Tang *et al.* [80], his team of researchers explored the CO<sub>2</sub> solubility, selectivity, and absorption capacity of poly(ionic liquid)s. From their study, it has been found that polymers from ionic liquid monomers had higher CO<sub>2</sub> absorption capacity than RTIL. According to Tang and his colleagues, this was the first discovery of polymers achieving greater CO<sub>2</sub> absorption compared to its monomers. Other notable characteristics observed from poly(ionic liquid)s were the fast CO<sub>2</sub> absorption/desorption and reversible capabilities [80]. In summary, Tang *et al.* proved poly(ionic liquid)s as a promising new alternative for CO<sub>2</sub> capture.

Lv *et al.* [84] carried out a study on functionalized ionic liquids. In this study, a new novel hydrophilic amino acid ionic liquid was designed and functionalized based on the imidazolium ionic liquid with glycine anions and hydroxy group. The advantages of this functionalized ionic liquid reported were easy synthesis process, high CO<sub>2</sub> uptake, good resistance towards O<sub>2</sub>, thermal stability, and efficient regeneration capabilities [84].

The above highlights some of the advances of ionic liquids being researched in the past decade.

# 4.3 Membranes

Generally, membrane separations are cost efficient methods of separating gases, when high purity gas streams are not of key concerns [85]. A summary from Yang's review paper regarding the progress in  $CO_2$ separation have concluded that membrane process is energy proficient, space saving, simple to scale-up, and could very well be the solution to a more efficient  $CO_2$  separation [45]. In this review paper, some of the possible precursor materials for membrane separation have already been mentioned, such as zeolites and poly(ionic liquid)s. Therefore, in this sub-topic, only a few notable membrane materials and technologies will be discussed.

Basically, the membrane materials for postcombustion  $CO_2$  capture can be divided into two main groups, namely, polymeric membranes and inorganic oxide membranes [86]. A simple discussion and an example of each group will be briefly introduced in this review paper.

# 4.3.1 Polymeric Membranes

Hollow fiber carbon membranes (HFCMs) are currently taking the limelight in the polymeric membrane technology for carbon separation. This strong interest for preparation of HFCMs is due to its enhanced selectivity and thermal and chemical stability [45].

One unique characteristic when discussing microporous membrane contactors is the capability of gas stream flow on one side and the absorbent liquid flow on the other side of the membrane, without phase dispersion. This sets it apart from conventional equipment, whereby problems such as flooding, foaming, and entrainment can be avoided. Other advantages include larger gas-liquid interfaces and the flexibility to scale up the prototype [87]. Due to these advantages of microporous membrane contactors, quite a considerable amount of academic and industrial research has been carried out to further understand and develop this technology. Qi & Cussler [88] were among the first to explore the possibility of utilizing microporous polypropylene membranes for CO<sub>2</sub> absorption [88]. A more recent investigation of HFCM for CO<sub>2</sub> absorption was carried out by He & Hägg [89]. He & Hägg prepared HFCM using cellulosic precursors and studied the various influences of operating parameters such as pressure, temperature, flow rate, and the composition of feed CO<sub>2</sub>. While it was concluded that the cost of this membrane technology is still high when compared to the current chemical absorption method, results from this research have also proved that the costs can be significantly decreased by reducing the carbon membrane wall thickness [89]. This suggests that HFCM still requires further optimization for potential CO<sub>2</sub> application in the near future. Therefore, it can be said that HFCM is still in the concept stage. This is further explained by Wang and his team, whereby they have observed that most HFCM studies and researches employ water, NaOH, or KOH solutions as absorbents in the membrane-based  $CO_2$  capture. This is possibly done to avoid complicated chemical reactions involved in the absorption to simplify the analysis [87]. However, this may cause complications as studies have shown that the wetting of membranes has its repercussions. A few studies showed that after prolonged contact with liquid adsorbents, or wetting of the membranes, the membranes suffered from various degrees of chemical and thermal stress which led to membrane swelling and morphological changes. These changes would elevate the mass transfer resistance and hence degrade the effectiveness of the membrane [90, 91].

# 4.3.2 Inorganic Membranes

Inorganic membranes, both porous and non-porous materials, have the upper hand of operating under high temperatures, which is a significant advantage when pre-combustion and post-combustion separation are of concerns [10]. Unlike polymeric membranes, which are more for commercial scale separations, inorganic membranes, such as ceramic and metallic membranes, are found in smaller scale separations [92].

One of the potential inorganic membranes is microporous silica membrane. This silica membrane utilizes a sieving effect via its small pores to separate CO<sub>2</sub>. Given that proper modifications on its amorphous structure are carried out, it can be a viable method for carbon separation with optimized CO<sub>2</sub>:N<sub>2</sub> selectivity [93]. A recent study made by Xomeritakis and his team [92] explored both the separation performance and stability of sol-gel silica-based membranes for CO<sub>2</sub> separation from flue gas. Their aim was to obtain silica membranes with both high CO<sub>2</sub> permeance and high CO<sub>2</sub>:N<sub>2</sub> selectivity. From the three types of silica membranes explored (pure, amine-derivatives, and nickel-doped sol-gel silica membranes), it was observed that pure silica membranes prepared under optimized conditions showed high CO<sub>2</sub> permeance and high CO<sub>2</sub>:N<sub>2</sub> separation factor. However, under high operating temperatures, the performance showed a sharp decline [92].

Yu et al. [94] has observed that there is a flaw to the inorganic membrane contactors, whereby diffusion resistance occurs between the membrane and adsorbents, and is significantly worse when membrane pores come into contact with liquid adsorbents. Yu and his team of researchers have observed this to be true for not only ceramic membranes, but membranes made from polymeric materials such as polypropylene (PP), polyvinylidene fluoride, polytetrafluoroethylene, polysulfone, polyether sulfone (PES), polyimide, and polyethylene (PE) as well. Therefore, a new superhydrophobic ceramic membrane was suggested and developed by Yu and his team. This new membrane design has the detrimental effects of wetting alleviated by periodic drying and a high CO<sub>2</sub> removal efficiency of >90% was observed [94]. A few researchers have also made studies to come up with hydrophobic membranes in an attempt to reduce the effects of membrane wetting. Some notable hydrophobic membranes attempted for CO<sub>2</sub> capture are modified hydrophobic aluminum oxide hollow

fiber membrane and hydrophobic polyether ether ketone hollow fiber membrane [95, 96].

An alternative method that has been explored is using metal membranes to concentrate CO<sub>2</sub> in flue gases. Metals suitable for this method need to have high hydrogen permeability. Therefore, those of the transition metal Groups IV and V and Pd are usually considered [97]. Palladium membranes are the most extensively studied among the metal membranes. This interest in palladium was explained by Buxbaum and Kinney [98], whereby the advantageous properties were highlighted in their research. Some of the properties include, good hydrogen transport efficiency, high selectivity even under elevated temperatures, resistant to corrosion and solvents, easy fabrication into tubes for hydrogen extraction units, and chemical resistance to carbon monoxide, steam, and hydrocarbons [98]. Recently, many newer researches were done to help support and further understand palladium membranes for  $CO_2$ concentration and capture in flue gases. Morreale and his team studied the permeability of bulk palladium at elevated temperature and pressure. Elevated temperature and pressure were chosen to simulate the conditions of process streams of CO<sub>2</sub> capture. The results showed that the permeability performance was comparable to those reported at lower temperature and pressure [99]. Other recent key researches to be noted were made by Douglas [100] which studied supported thin-film palladium membranes and palladium/copper alloy composite membranes. The researches reported positive outcomes and viability of metal membranes for flue gas concentration and separation purposes.

Palladium membranes, however, still require modifications as it is far from flawless. Its many flaws prevent it from commercialization and are not ready to be installed in major point sources for carbon capture. Some of the common disadvantages reported are high costs, corrosion problems, and stability concerns. Furthermore, a challenge still exists, whereby methods to produce thin and detect free palladium membranes are yet to be discovered [97].

# 4.4 Cryogenics

The last method of  $CO_2$  capture to be discussed in this paper is the cryogenic separation method. This is a unique separation method whereby it utilizes the difference in boiling points of various gas species to separate them. Mainly, it separates  $CO_2$  (which condenses at a low temperature of -56.6°C at atmospheric pressure) from the flue gas stream by condensation [11]. The process of cryogenic separation of flue gas comprises of a series of steps, which are compression, cooling, and expansion. All these steps are carried out on the basis of the differences among the phase transition properties of the components or gases in the flue gas [101]. This method has gained interest and devotion from many researchers as it has a few distinct advantages. The advantages of cryogenic separation can be summarized as the following [102]:

- 1. Enables direct production of liquid CO<sub>2</sub> for easy storage and transportation.
- 2. A straight-forward technology which requires no solvents or any other components.
- 3. Easy scale up from lab-scale to industrial-scale.

Many researchers did studies on the cryogenic method with the aim of achieving high  $CO_2$  capture/separation rates and lower the energy penalties. Some of the recent developments are listed and briefly discussed below.

Tunier *et al.* [103] worked on a novel  $CO_2$  capture based on this cryogenic method. Tunier and his team demonstrated a process for cryogenic  $CO_2$  freeze-out using dynamically operated packed beds to separate N<sub>2</sub>/CO<sub>2</sub> mixtures. The experiment showed positive results where a good separation was observed. Furthermore, Tunier also made simulations which showed good resemblance to the experiment [103].

Song et al. [104] has designed a new cryogenic capture method based on the commercial Stirling Cooler. Song and his team attempted to address the high energy consumption of cryogenic CO<sub>2</sub> capture by incorporating a new cryogenic system based on the Stirling Cooler [104]. Other significant advantages of the Stirling Cooler are high efficiency, high reliability, and small size [105]. The Stirling Cooler operation contains 4 distinct processes: expansion under an isothermal condition, refrigeration under a constant volume condition, compression under an isothermal condition, and heating under a constant volume condition [106]. Based on this new cryogenic capture method with the Stirling Cooler system, Song and his team has achieved good CO2 recovery results with up to 96% recovery and 1.5 MJ/kg CO<sub>2</sub> consumption. These are promising results, however, CO<sub>2</sub> capture from flue gas is yet to be tested [104].

Xu *et al.* [101] analyzed the phase transition of both  $CO_2$  and mixtures of  $CO_2/H_2$  with the aim of proposing a novel cryogenic separation method. In Xu's research, a system which consisted of a twostage compression, two-stage refrigeration, and twostage separation was adopted. As a result, high  $CO_2$ recovery and purity could be achieved with a low energy penalty [101].

Another similar study was made by Besong *et al.* [107], whereby a cryogenic system which comprised of a compressor and a flash unit was proposed to reduce the energy penalty. Furthermore, this study has also evaluated the low temperature

process with the aim of producing high purity and high pressure  $CO_2$  output by means of simulation and modeling [107].

Despite the many advantages coupled with the developments in the cryogenic separation technology, there are still many obstacles to be overcome before this technology reaches its full potential. The main concern of the cryogenic separation method is the large amount of energy required to keep the system cool [13]. This causes it to be highly cost ineffective. Hence the various researches and developments made tend to look into this problem, aiming to reduce the energy penalty [101, 107]. Furthermore, cryogenic separation relies on the assumption whereby the flue gas contains only CO<sub>2</sub> and N<sub>2</sub>[13]. If other gases such as H<sub>2</sub>O, SO<sub>x</sub> and NO<sub>x</sub> are found in the feed stream, it will severely interfere with the cooling process, leading to formation of solids which may clog the equipment and also reduces heat transfer rates [108]. This means that an extra step is required to remove all other components found in the flue gas stream.

However, the fact that the cryogenic separation method is able to achieve a very high CO<sub>2</sub> recovery (may even exceed 99.95% after distillation), makes it an interesting alternative for CO<sub>2</sub> capture [108]. This keeps it on the table and researchers continue their exploration into this technology to further optimize it. Currently, cryogenic processes are used in special circumstances and also in hybrid systems [13, 108].

#### CONCLUSION

In the beginning of this review paper, the challenges for  $CO_2$  capture were highlighted, and the different approaches, namely pre-combustion, oxyfuelcombustion and post-combustion, were discussed. From the three approaches presented, it is foreseeable that the post-combustion approach is the most viable option. As mentioned in the beginning, postcombustion capture is not only simple in terms of design, but more importantly, it can be easily integrated into existing plants thus providing a cheap and instant improvement.

Then, this review focused on the 4 main technologies and materials that have emerged in the past decades. For each technology, different materials and methods utilized by different researchers were analyzed. Their efficiencies were determined in terms of  $CO_2$  selectivity,  $CO_2$  uptake capacity, cost, and advantages and disadvantages to be considered. Taking these factors into considerations, it is unfortunate to report that, currently, no single unique solution exists when it comes to the  $CO_2$  capture problem. Therefore, this review not only serves as a highlight of recent emerging  $CO_2$  capture progress, but also helps narrow the search for a better  $CO_2$  capture technology.

From the different post-combustion CO<sub>2</sub> capture methods, the activated carbon adsorption method seems to be the most cost efficient. This is due to the cheap and abundant raw materials and precursors. It can also be easily retrofitted into most existing plants. However, it is less efficient in terms of selectivity and overall CO<sub>2</sub> uptake capacity. Its zeolite and ZIF counterparts are more expensive but show better selectivity and adsorption. Nonetheless, its true potential lies in its ability of hybridization with other potential materials to improve its capabilities. This is supported by many new notable researches, which aimed to combine activated carbon, zeolites, and ZIFs with other materials to enhance their capabilities. While most of these researches were not aimed for CO<sub>2</sub> capture, the possibilities exist whereby a hybrid adsorbent may be discovered, which consists of superb capabilities.

The sequestration and transportation of  $CO_2$ are considered to be relatively mature and stable, but yet no operating commercial-scale CCS projects are to be found. This is because of the most important component,  $CO_2$  capture, has yet to be established. I hope that this review article would not only contribute, but also serves as a motivation to the scientific community to work towards a solution to the  $CO_2$ capture problem.

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