A REVIEW OF PRE-COMBUSTION CO$_2$ CAPTURE IN IGCC

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Abstract

Integrated Gasification Combined Cycle (IGCC) with Pre-combustion has many advantages over post and oxy-combustion systems. This is because the CO$_2$ *will be at higher pressure (requires smaller equipment) thereby making the separation process efficient and easy for sequestration. However the challenges remain to exploit this technology are; (i) it can only be applied for new plants since the separation process becomes integral part of combustion (results in higher down times), and existing plant cannot be retrofitted, (ii) the technology is not as mature as other counterparts and cannot be applied for large scale power production, (iii) higher energy penalty due to cooling of syngas for* CO$_2$ *separation with conventional methods.*

These issues have led worldwide researchers to focus on overcoming the challenges and make the technology of future. From the research of past decade, it is evident that CO$_2$*separation by adsorbents is best choice. Due to inherent disadvantages of process such as limited operating temperatures, recovery and purity of* CO$_2$, *recovery &regeneration energy penalty, much of research in focused on developing enhanced adsorbents and processes. In this paper we present different techniques and materials developed by researchers in the past decade and also present future scope for pre-combustion capture applied to IGCC.*

Keywords: pre-combustion, post-combustion, oxy-combustion, adsorption, CO$_2$ *capture, IGCC*

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INTRODUCTION

Gasification is the most efficient and cleanest technology for utilizing the carbonaceous fuels like coal, petroleum products, biomass, etc. Coal being most abundant and utilized among all these fuels, is the most contributing one to environmental pollution through emission of greenhouse gases (GHGs) such as CO$_2$, NO$_x$ and SO$_x$ and in turn to global warming. Capturing CO$_2$has received much attention by the researcher across the world because of its detrimental effects on environment. Its atmospheric concentration has increased from a pre-industrial level of 200ppm to 384ppm in 2007 and is expected to reach 550ppm by 2050 even if the emission levels are stable for next four decades [1].

Recently there has been rapid growth in funding by government agencies and research activities worldwide for CO$_2$capture, storage and utilization. Since the most contributing point sources are power plants, the target systems for many of the researchers are Pulverized Coal (PC), Natural Gas Combined Cycle (NGCC) and Integrated Gasification Combined Cycle (IGCC). While the first two systems are older, well established and mature technologies, IGCC is still nascent and lots of improvements are needed for the betterment of plant performance both in terms of efficiency and CO$_2$capture.Three main methods for CO$_2$capture are: pre-combustion, post-combustion and oxy-combustion (Figure 1) [6]. In all these methods the CO$_2$capture performance depends primarily on the CO$_2$partial pressure and concentration. Post-combustion and Oxy-combustion methods are based on

CO$_2$capture from flue gases. The main disadvantage of CO$_2$capture from flue gases is presence of impurities and low concentration of CO$_2$in the presence of nitrogen. Typical concentration of CO$_2$is 5 vol% for NGCC and 15 vol% for PC [2]. Not all systems are compatible with all capture methods: For example, Pre-combustion is mainly suitable for IGCC [3], where a high pressure is used to separate CO$_2$by physical absorption, Post-combustion and Oxy-combustion for PC system where as all the three methods can be used for NGCC system. In this paper we presented various methods of CO$_2$capture for the target systems with particular focus on IGCC with pre-combustion.
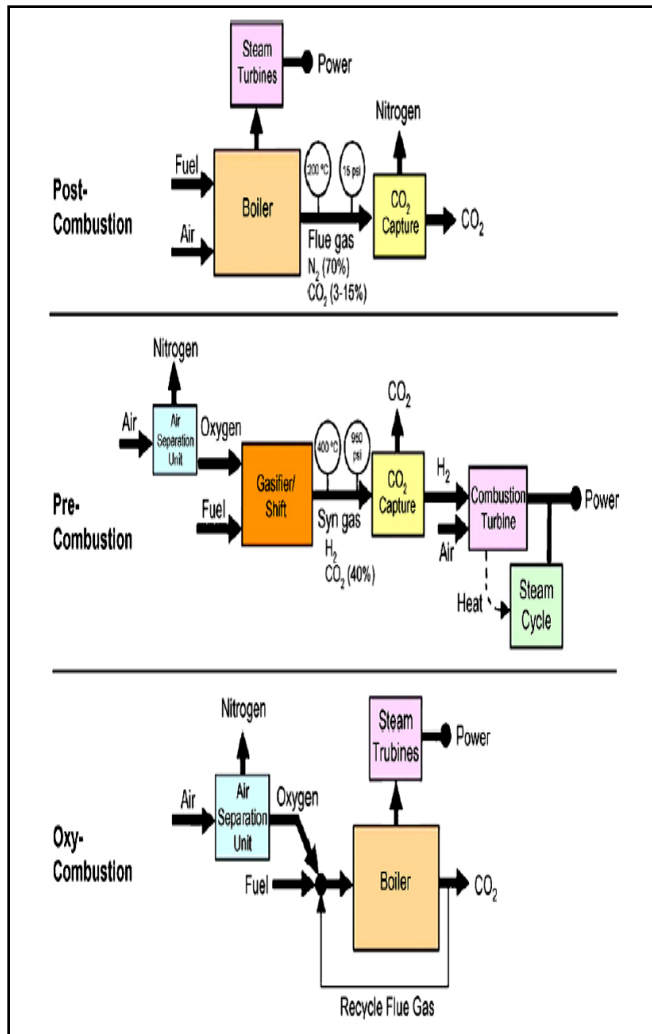
Fig-1 Block Diagrams of various capture methods [6]

2. PRE-COMBUSTION CAPTURE:

Pre-combustion CO_2capture related to a gasification plant is shown in Figure 2. In a gasification reactor, the amount of air or oxygen (O_2) available inside the gasifier is carefully controlled so that only a portion of the fuel burns completely. This "partial oxidation" process provides the heat necessary to chemically decompose the fuel and produce synthesis gas (syngas), which is composed of hydrogen (H_2), carbon monoxide (CO) and minor amounts of other gaseous constituents. The syngas is then processed in a water-gas-shift (WGS) reactor, which converts the CO to $CO_2$and increases the $CO_2$and H_2 mole concentrations to about 40 percent and 55 percent, respectively, in the syngas stream.

At this point, the CO_2has a high partial pressure, which significantly improves the driving force for various types of separation and capture technologies. After CO_2removal, the H_2 rich syngas can be converted to power. Because the gasification process is operated at high pressure and $CO_2$is

present at much higher concentrations in the syngas (i.e., in comparison with post-combustion flue gas), pre-combustion CO_2capture has the potential of being less expensive than post-combustion CO_2capture. For the same amount of CO_2captured, a much smaller volume of gas needs to be treated, leading to much smaller equipment size and lower capital costs.
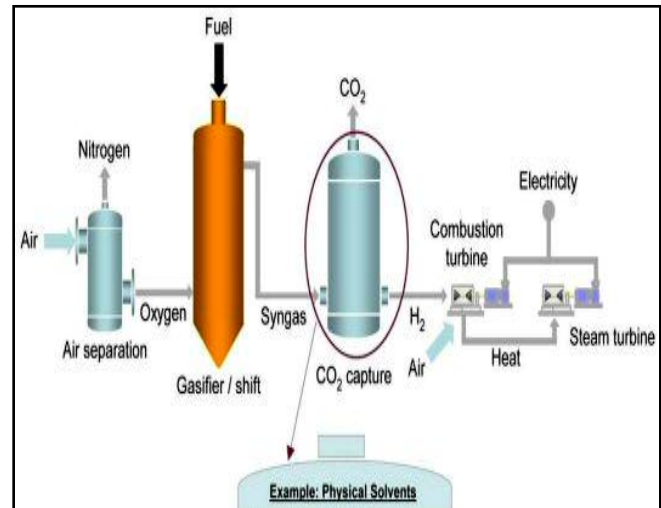

Fig-2 Pre-combustion CO_2capture (Source: www.netl.doe.gov)

The main challenges related to pre-combustion CO_2capture at this time stage are;

1. High capital cost due to its applicability only for new power plants where the capture process has to be an integrated part of the combustion process. Existing plants that will be retrofitted with CO_2capture will mainly opt for post-combustion capture.
2. Pre-combustion technologies like IGCC are not as mature as post-combustion capture and oxy-combustion technologies.
3. Gas turbines running on hydrogen are a huge challenge.

One of the main capture methods applied to CO_2separation is amine scrubbing. The potential limitation for this process is that the liquid scrubbing must occur at relatively low temperature [4]. This requires cooling of gas coming from WGS for CO_2capture and reheating again before sending to turbine block. The cooling and reheating of gas adds to substantial energy penalty and reduces cycle efficiency. In the following section we have presented various capture/separation methodologies applied to pre-combustion capture and enlisted the significant contributions made by the researchers across the globe and tabulated them in a lucid manner.

3. CAPTURE METHODOLOGIES

The basic methods for CO_2separation are based on Sorbent/solvents, membranes, adsorption and cryogenics.

Cryogenics is not a contender because of its high energy requirements and not feasible for low and moderate CO_2concentrations. These techniques are shown in Figure 3.

Solvents like Mono-ethanolamine (MEA),N-methyldiethanolamine (MDEA) are widely used for CO_2 capture with a recovery rate of 98% purity can be achieved. The main disadvantages of this process are high energy requirement during desorption, rate of degradation of solvent [7]. In case of IGCC with pre-combustion capture where the concentration and pressure are much higher, physical solvents like Selexol is best choice [5]. The advantage of this process is captured CO_2 can be released by depressurization thereby avoiding high heat consumption of amine scrubbing process.
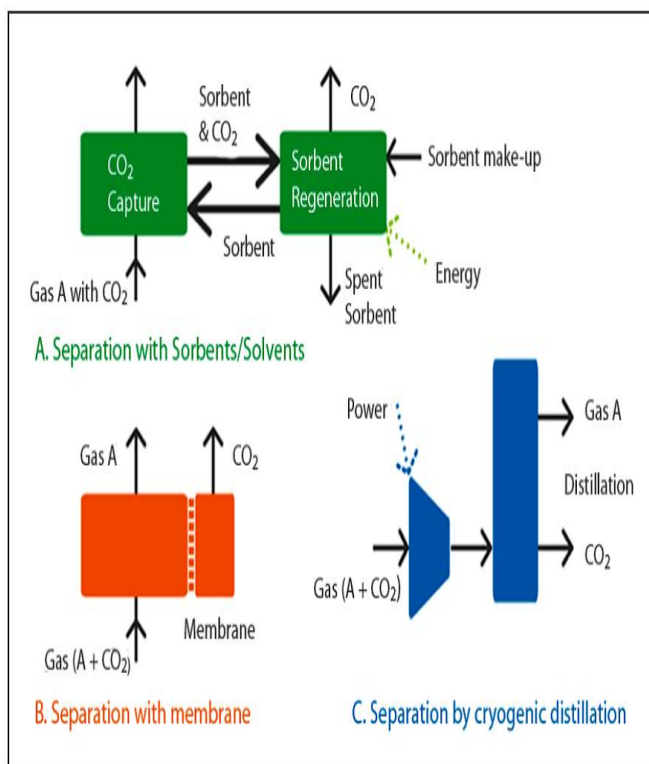

Fig-3 Basic methods of CO_2 separation (Source: www.CO$_2$captureproject.com)

The adsorbent based separation methods are Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA). These techniques are widely used in the power plants and oil refineries to separate gases like CO_2, H_2S etc. The principle of these methods is based on decreasing pressure (PSA) or increasing temperature (TSA) to regenerate the adsorbed gases. The typical PSA process is shown in Figure 4.
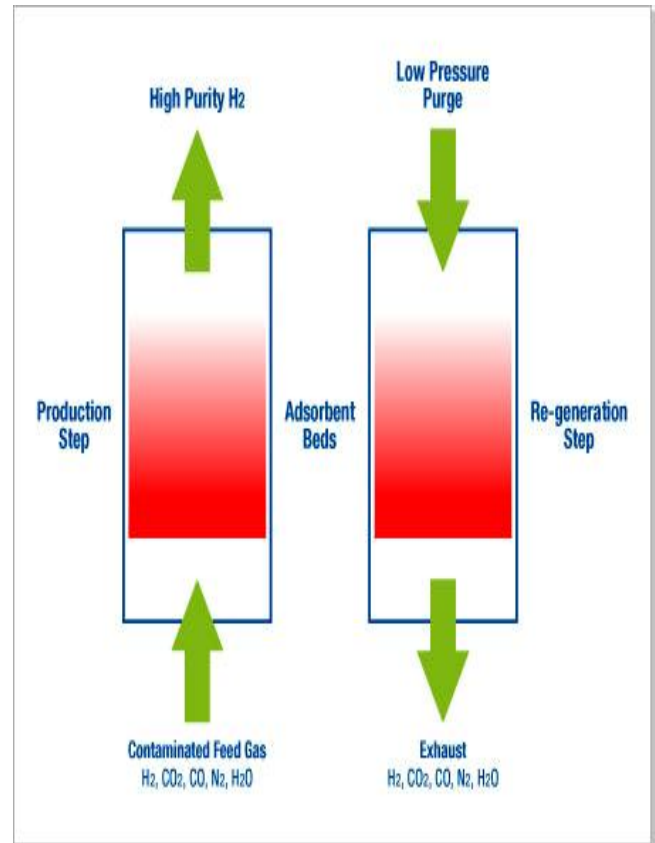

Fig-4 Pressure Swing Adsorption (Source: www.xebecinc.com)

Membrane separation is based on allowing one component of gas to pass through while others not. Various types of membranes such as inorganic membranes, palladium membranes, polymeric membranes, Zeolites are commonly used. Membranes are not popular mainly because they cannot achieve high degree of separation. Recent advancement in membrane bases technique is solvent assisted membranes.

In the IGCC plant, the typical operating temperature is 250-450°C. This operating window poses significant challenges for CO_2capture as there were no regenerable sorbents with sufficient CO_2removal capacity at 250-350°C, according to Siriwardane et al [10]. R.Singh et al [4] have investigated on range of materials suited for low and high temperature applications. According to them, carbon based absorbents and Zeolites are suitable up to 120°C, lithium based materials for elevated temperatures between 500-700°C. They have characterized the absorbents based on different properties and process requirements and presented the results in Table.1 which shows experimental results on different adsorbents, with different components at 1bar.

Table 1: Experimental results on different adsorbents, with different components at 1bar

materials	Temp °C	CO₂ mol/kg	CO₂/N₂ Sel.	H₂S mol/kg	NH₃ mol/kg	H₂O mol/kg	Comments*
13X	120	2.62	29	1.85	4.0 [9]	11.4	H₂S: loads and unloads reversibly; NH₃: strongly loads (TSA required for regeneration); H₂O loads, strong vacuum or heating required for desorption.
	200	0.67	-	-	-	13.9 ‡	
CaCHA	120	2.79		-	-	16 (30°C)	H₂O: very difficult to unload (vacuum or heating required); H₂S: unloading difficult; CO loads slightly (reversible)
	200	1.09	27	3.91	0	TBA	
	400	0.61				-	
HTC	300	0.20	"High"	1.79	0.02	very low [10]	H₂S: regeneration difficult; NH₃: readily regenerated
	400	0.46	"High"				
Mg-Na DS†	375	4.70	"High"	1.74	0	TBA	H₂S: unloading difficult
Mg-K DS	375	1.5	High	2.08	0	TBA	
LDO	200	1.2	>100			0.94	Tests carried out with SOx in post combustion flue gases show that SOx preferentially sorbs on LDO [11]

+ water data collection under actual precombustion conditions is to be undertaken.

* loading and unloading under partial pressure swing conditions.

† DS = double salts; reproducibility difficult.

‡Data from UOP: Water measured on 13 X , 1 bar water partial pressure

According to their work, 13X is good in the temperature range of 200°C, HTC for elevated temperature in the range of 375°C and TSA with double salt adsorbents are suitable for 375-400°C.

Jan WilcoDijkstra and team [22] of Energy Research Center of Netherlands have worked on developing new membrane reactor technology for NGCC (Natural Gas based Combined Cycle). The working principle of membrane technology is shown in Figure.5. Two distinct membrane reactors are membrane reformers (M-REF) and membrane water-gas shift reactors (M-WGS). In the M-REF steam methane reforming reaction (SMR) takes place resulting in retentate of CO₂ and H₂O. In the M-WGS reactor the reaction between CO and H₂O takes place and H₂ is separated from the Membrane.
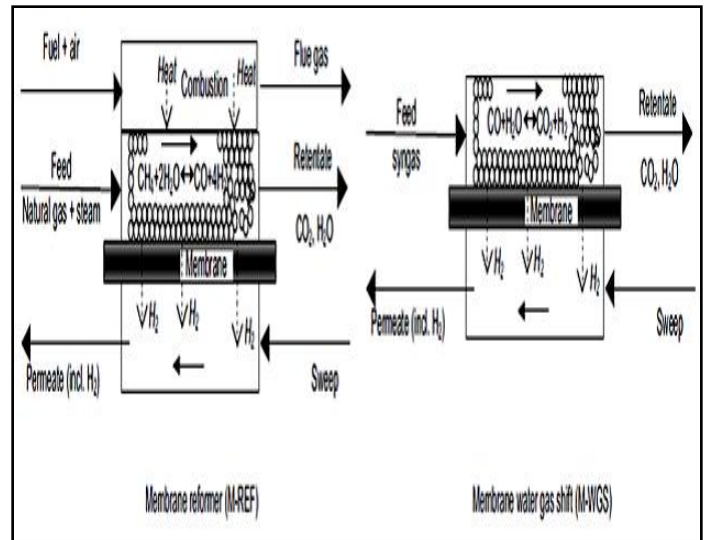

Fig-5 Membrane technology developed for pre-combustion CO₂capture of NGCC plant [22]

The test results of reactors indicated that increasing feed pressure the conversion is increased (Figure.6), which is a direct result of the increase of hydrogen recovery with pressure, shifting the reaction to higher conversion.
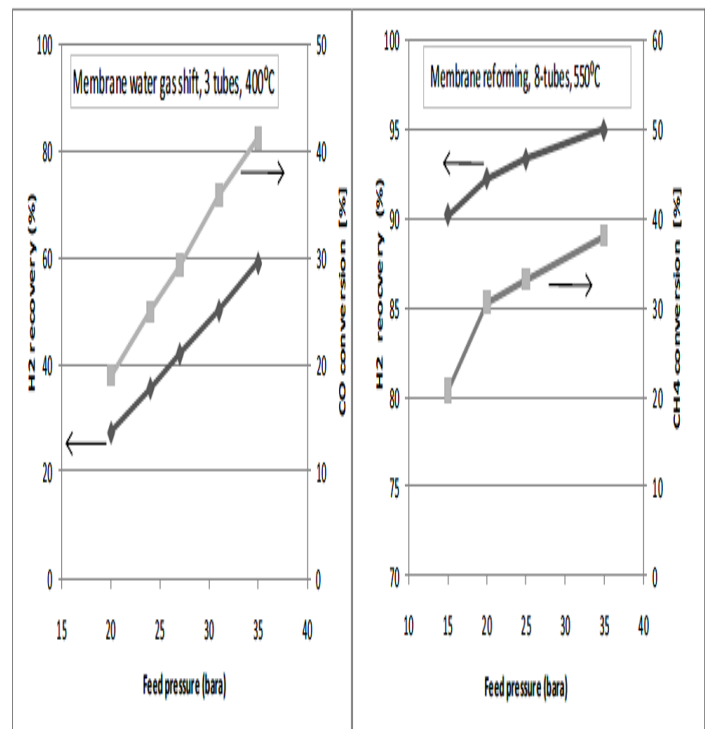

Fig-6 Variation of Hydrogen recovery and CO conversion with the feed pressure [22]

Y.Seo, et all [8] have investigated the usage of silica gel pore structure with water for CO_2 separation and effect of CO_2 concentration on dissociate pressure with silica gel pores of different sizes was also studied. The simulation results have indicated that 100 nm pore size has resulted in gas stream containing maximum of 96 mol% of CO_2 with one-stage reactor. They have also investigated the gas hydrate formation on fixed bed type reactor with silica gel pores with water and demonstrated substantial increase in the extent and rate of hydrate formation with the silica gel pores with water which can be a promising technique for pre-combustion CO_2 capture.

Gongkui Xiao, et al [9] have worked on developing adsorbents suitable for CO_2 capture from syngas at higher temperatures corresponding to operating temperatures of IGCC at the exit of typical water gas shift reactor. The proposed adsorbents are based on double salts of $MgCO_3$ and K_2CO_3 with varying ratios of Mg: K which is characterized by X-ray diffraction analysis. The experimental results indicated that the adsorption amounts are highest in the temperature range of 350-375°C with CO_2 adsorption amount of 8.5 wt% and thus making this method a potential candidate for CO_2 capture in IGCC. The adsorbents have also exhibited excellent stability both in PSA and TSA operations.

Andrew Wright, et al [11] as a part of CACHET project have developed new process, Sorption-enhanced water gas-shift (SEWGS) and demonstrated that it is a potential process for pre-combustion capture at higher temperatures thereby reducing the energy penalty and overall cost. Sorption-enhanced water-gas-shift (SEWGS) is a novel pre-combustion capture technology that has the potential to reduce CO_2 capture costs compared to conventional removal processes such as amine scrubbing. The process combines CO_2 adsorption with the high-temperature water-gas-shift reaction (HTS). A packed bed of iron-chrome is used to catalyze the reaction with a typical feed temperature in the range of 370-400°C (Twigg [12]). The conversion equilibrium of CO problem at HTS operating temperature is solved by the use of SEWGS.

While many researchers are working for enhancements and developing new techniques & materials, the some significant contributions of distinct nature during the past decade are listed in Table 2.

CONCLUSION

Adsorbent based techniques proved to be best option of pre-combustion CO_2 capture. Adsorbents for wide range of temperatures have been developed, for example Carbon Nanotubes (CNTs), Zeolites, MOFs for low temperature (<200°C) applications, Layered Double Hydroxides (LDHs), Hydrate based adsorbents for intermediate temperatures (200-400°C) and Calcium and Ceramic based adsorbents for high temperatures (>400°C). MOFs particularly provide better process control, high storage capacity and low recovery heat. Wide varieties of MOFs have been developed to address varying industrial needs. Another effective technique is PSA based membrane separation. Membranes are particularly suitable for high pressure and temperature applications. The inherent disadvantages of membranes being slow recovery and increased degradation can be overcome by hybrid techniques. Solvent assisted membranes, hydrate formation coupled with membrane technique are some of the promising avenues for further research. SEWGS is another promising frontier in which shift reaction takes place in reactors to separate CO_2. The effect of different catalytic materials and operating parameters to enhance the reaction can be studied further. Key requirements of adsorbents like operating temperature window, selectivity to CO_2, stability, regenerability, energy penalty, etc have opened more research avenues for developing better adsorbents.

Table.2 Significant developments of distinct nature during past decade

Research Team	Year	Objective	Methodology	Result	Ref.
A Lyngfelt, et al	2001	Chemical Looping Combustion (CLC)	Metal oxide oxygen carrier is used to supply oxygen required for combustion, and separating combustion products CO_2 and H_2O. The reduced metal oxide is subsequently oxidized with air.	Very less amount of energy is required for CO_2 separation. The process is faster and yields higher concentration CO_2 for easy capture and sequestration.	13
Willis, et al	2006	Metal organic frameworks (MOF)	Metal organic frameworks (MOFs) are a new class of hybrid material built from metal ions and organic bridging ligands are used for adsorb CO_2.	High storage capacity is possible, and the heat required for recovery of the adsorbed CO_2 is low. MOF-177 has shown one of the highest surface areas and adsorption capacity for CO_2 at elevated pressure.	14
Praveen Linga, et al	2007	Hydrate formation coupled with membrane separation	Hydrates are used along with membranes	Hydrate crystal formation from CO_2/N_2 mixtures showed that CO_2 prefers the hydrate phase. CO_2 recovery was found to be 36.7–42.1% in one stage at 11.0 and 10.0MPa.	15
T.C.Drage et al	2009	Development of Activated Carbon based adsorbents	Effect of porosity of phenolic resin (Novolak) beads on CO_2 capture	Maximum CO_2 adsorption capacity of 58 wt.% (13 mmol g-1) at 3 MPa	16
David J. Heldebrant, et al	2009	CO_2 Binding Organic liquid (CO_2BOL)	CO_2BOLs are used for CO_2 absorption and the energy requirement for recovery of CO_2 is studied	Free energy requirement for binding is CO_2 is small and independent of alcohol. Since the specific heats of CO_2BOLs are about 50% lower than water based amines, lesser energy is required for recovery of CO_2.	17
Soodabeh, et al	2012	Separation of CO_2 by Multiwall Carbon Nanotubes (MWCNT)	Adsorption of CO_2 by MWCNT was investigated at 218-318°C and 40 bar.	Temperature has no significant effect on H_2 when compared to CO_2. Higher pressure and lower temperature increases the CO_2 adsorption. This differential adsorption is a promising tool in future.	18
R.ScottAlvis, et al	2012	Improving adsorption characteristics of MDEA	Piperazine is used as promoter for CO_2 adsorption which increases the reaction speed. Effect of solvent strength, MEDA-piperazine composition and temperature are studied	CO_2 adsorption is very sensitive to piperazine content (Amine strength worsens the absorption due to higher viscosity. Adsorption of CO_2 increases with temperature till 50°C and suddenly decreases beyond.	19

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