2011

Co2 Adsorption On Solid Sorbents

Bingyu Li
University of Mississippi

Recommended Citation

Li, Bingyu, "Co2 Adsorption On Solid Sorbents" (2011). *Electronic Theses and Dissertations*. 918.
https://egrove.olemiss.edu/etd/918

CO_2 ADSORPTION ON SOLID SORBENTS

A Thesis
Presented for the
Master of Science Degree
Chemical Engineering
The University of Mississippi

by

Bingyu Li

August 2011

ABSTRACT

Sorbent-based CO_2 capture technology is considered as one of the potential scientific techniques for mitigating greenhouse gas emission. Major advantages of sorbent based adsorption are its low regeneration energy coupled with the elimination of corrosion and equipment degradation characteristic of amine based solvent CO_2 capture systems which are the preferred industrial methods.

Different CO_2 capture configurations, processes, and operational parameters for different sorbents were reviewed and summarized. Efficient industrial applications for CO_2 capture require that solid sorbents possess an adsorption capacity between 1000-2000μmol/g or more together with a long-term regeneration capacity. Economical consideration necessitates that the cost of CO_2 sequestration be less than $10 per ton of CO_2. Scientific literature identifies various kinds of sorbents, examples include: activated carbon, modified activated carbon, zeolite, metal-organic framework (MOF) and amine grafted sorbents on silica support. Literature review reveals that amine-grafting process can boost CO_2 adsorption on silane sorbent support. The larger surface area of the sorbent support means a greater number of active sites available for grafting which results in a higher CO_2 adsorption capacity. The presence of water vapor in the gas stream during grafting and/or during CO_2 adsorption can also improve CO_2 adsorption of amine-grafted sorbents.

Huang reported that MCM-48 silica grafted with 3-aminopropyltriethoxysilane had the greatest CO_2 adsorption capacity under anhydrous conditions with 2.30mmol/g sorbent. While

Harlick reported that TRI-PE-MCM-41 had the greatest CO_2 adsorption capacity under wet conditions with 2.94mmol/g sorbent.

DEDICATION

This thesis is dedicated to my mother, aunt and Yisha who always support and encourage me in every way through all my life.

ACKNOWLEDGMENTS

I would like to show my sincere gratitude to everyone that has helped in making this work possible. First I would like to thank my supervisor, Prof. Wei-Yin Chen for affording me the opportunity to work with him, as well as his timely guidance, advice, encouragement and patience all through my study at Ole Miss. I would also like to thank my thesis committee members: Dr. Ajit Sadana and Dr. Clint Williford for the time devoted for my thesis, for their help and advice during the graduate coursework. And I would like to extend my thanks to the entire faculty and staff in the Department of Chemical Engineering for making my experience here valuable and enjoyable.

To my colleagues, Guang, Swetha and Eneruvie, I am grateful to you for helping out in the lab. My gratitude also extends to the undergraduate students, Patrick and Corbett, who carried out the experiment with me. And I also would like to thank Mei Wang, who helped me in resolving problems encountered in one of the instrument used in my studies. You are all very much appreciated.

I remain indebted to my family who has all toiled to see me through my years of academic formation and set me on the path of becoming an achiever in life. I am very grateful to them for their support and love all through my education. My heartfelt thanks also go to my friends, David, Carol, Xiaofei and Xiaoning, who always encouraged and supported me. Finally I would like to appreciate Mrs. Chen for her help, advice and support all through my stay at Ole Miss.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

Greenhouse gases (GHG) are gases in the atmosphere that allow solar radiation to reach the earth's surface but trap thermal radiation leaving the earth's surface [1]. With the exception of water vapor, these gases are present in trace amount in the atmosphere. According to the Kyoto Protocol [1], the most commonly reported greenhouse gases include:

- Carbon dioxide (CO_2)
- Methane (CH_4)
- Nitrous oxide (N_2O)
- Hydrofluorocarbons (HFCs)
- Perfluorocarbons (PFC)
- Sulfur hexafluoride (SF_6)

These gases enter the atmosphere both as part of the natural cycle and as a result of human activities (mostly fossil fuel use) [1].

According to DOE's Energy Information Administration (EIA) report, fossil fuel accounts for approximately 71 percent of the current total US electricity generation. Thus over 40 percent of the 5.8 billion metric tons of total US anthropogenic CO_2 emission was produced [2]. Of this figure, coal based power plants currently accounts for about 50 percent of US electricity generation (see Figure 1-1), and this is expected to continually play an important role in the national electricity generation in the foreseeable future [2].

DOE's Energy Information Administration (EIA) also projects that the current 308GW electricity generation of coal-based power plant is expected to increase to approximately 323GW by 2030 [2].

Recent concerns about the anthropogenic emission of greenhouse gases such as CO_2 and its adverse effect on the global climate change, place electricity production from coal-based power plants to be under serious scrutiny. Thus, federal legislation/regulation could be enacted that would limit CO_2 emissions from the US power sector in addressing these concerns [2].

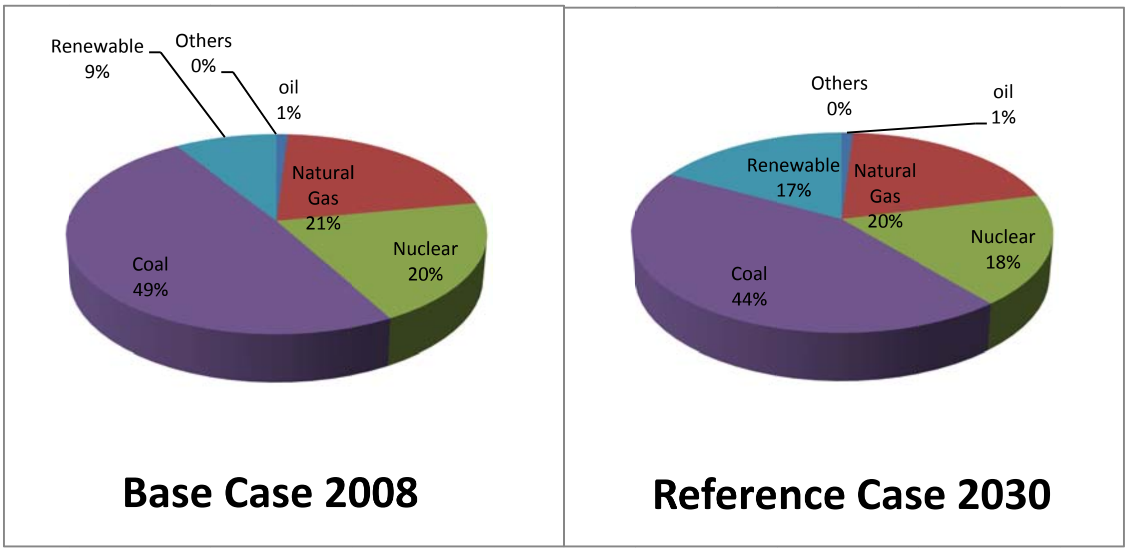


Figure 1-1: US Electricity Generation by Fuel Type [2]

Figure 1-2 reveals three major sources of US anthropogenic CO_2 emissions i.e. by fuel type. Of this breakdown, Coal-based power plants which currently consume over 1 billion metric tons of coal, produces approximately 1.9 billion metric tons of CO_2 emission which comprises 37 percent of the total US anthropogenic CO_2 emissions [2]. Moreover, EIA estimates that 95 percent of the CO_2 emission from coal-based power plant to be released from date till 2030 is projected to come from existing and new coal-based power plants, thus making this sector a major target for reduction should federal legislation/regulation be enacted in reducing CO_2 emission from the power sector [2].

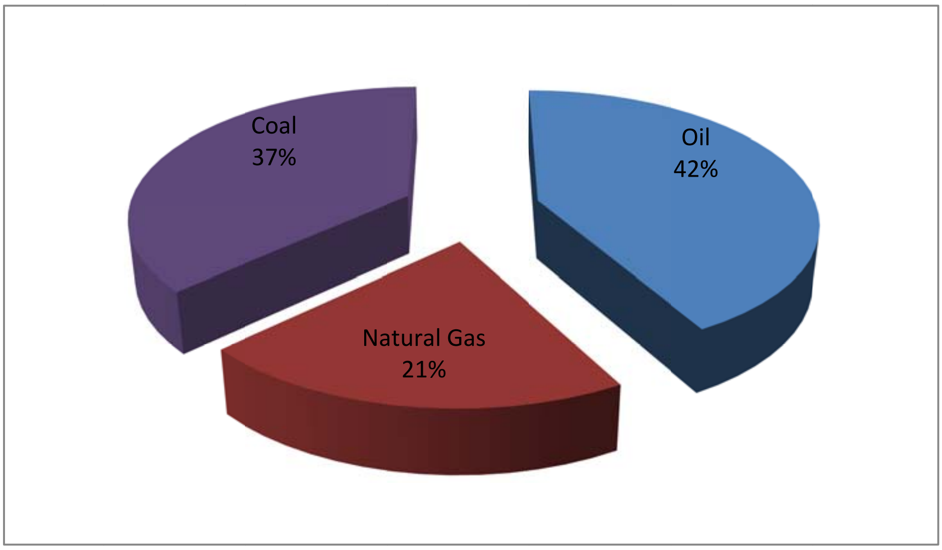


Figure 1-2: Source of US CO_2 Emissions by Fuel Type in 2008 [2]

Zhang et al.[3] in their report stated that fossil fuel supplies accounted for 85 percent of the world's energy needs and that as a result of the world's heavy reliance on fossil fuel coupled with the ever increasing emission of large amount of GHG (CO_2 among others) from this source, the ambient concentration of CO_2 is projected to increase from about 280ppm dating back to the pre-industrial revolution period (1900s) to about 450ppm by 2050 if actions are not taken or put in place to mitigate GHG emissions.

In this light, several options have been considered and are being considered in either:

- Decreasing CO_2 emission from the power/other sectors or
- Improving the efficiency of energy use

by increasing the use of low carbon energy sources as potential ways of reducing CO_2 emission from these sectors. Some of these options include:

- Increases in nuclear and renewable energy supplies [2] and
- Implementation of carbon capture and storage (CCS) on coal, oil, and natural gas power plants [2, 3].

DOE/NETL[2] and other scientific organization or experts such as Environmental Protection Agency (EPA), the Electric Power Research Institute (EPRI), and the Intergovernmental Panel on Climate Change (IPCC) – believe CCS presents the sole practical option in achieving considerable reduction in CO_2 emission from the various fossil fuel power plants [2,3].

Carbon Capture and Sequestration technologies option is fast becoming a major issue being addressed by the scientific community. The CCS process involves three major steps:

- CO_2 capture and concentration of the CO_2 produced either from the industries or other energy related sources [2, 4]
- Compression and transportation [2]
- Storage i.e. away from the atmosphere for a long period of time [2, 4].

In a coal-based power plant, three general categories of CO_2 capture technologies are applied [2], namely:

- Pre-combustion
- Post-combustion and
- Oxy-combustion

Research in the area of carbon capture involves several technologies such as sorbent-based separation (adsorption) [3], solvent-based separation (e.g. amine-based absorption), cryogenic separation and membrane-based separation [2, 3].

CO_2 capture via sorbent-based technologies has been identified as one of the potential scientific techniques for greenhouse gas emission [3]. The success of this technique is dependent on the development of:

- A low cost adsorbent with
- High selectivity and
- High adsorption capacity

Along this path, DOE/NETL's CO_2 capture overall goal is to "develop advanced technologies to achieve 90 percent CO_2 capture at less than 10 percent increase in the leveled cost of energy (COE) of pre-combustion capture for integrated gasification combined cycle (IGCC) power plants and less than 30 percent increase in COE of post- and oxy-combustion capture for new and existing conventional coal-fired power plants."

With the exception of plants located directly above geological formations, captured CO_2 at the point of capture can be transported to its storage site either through [1,4]:

- Pipeline or

- Via ship, rail and roads (tank cars).

Transportation through pipelines is a more common method in conveying CO_2 to its storage site. In doing this, CO_2 is compressed above 8MPa in order to avoid two phase flow regimes thus, increasing the density of the gas and in effect making it cheaper to transport [4]. In transporting CO_2 via ships, rail or road, the vessels used are insulated at temperature below ambient and at a much lower pressure [4].

Finally, storage of the captured CO_2 could be in:

- Aquifers (Saline formation) especially oceans and seas [5]. This could be done either by increasing microalgae biomass or using $CaCO_3$ like coral reefs.
- Depleted oil and gas fields (underground reservoirs) [1, 5] and
- Unmineable coal seams [1].

The object of this study is the review of the various sorbents for CO_2 capture in flue gas, review the importance of the various cost-effective advanced CO_2 capture technologies on the existing or new coal based, natural gas or oil fired power plants, and recommend an optimal sorbent based on cost of energy (COE) with low cost, high CO_2 selectivity and adsorption capacity.

2 LITERATURE REVIEW

2.1 Sorbent Characterization

Yang [6] reported that all microporous materials could serve the all-important purpose of being used as sorbents for gas and liquid purification and separation. Examples of these include: chars from bones, biomass, coal, calcined clays, iron oxide, calcined bauxite etc. Sorbents are broadly characterized in terms of their physical and chemical properties. In the use of sorbents for adsorption purposes, the physical properties of the sorbent plays a more important role compared to its chemical properties.

Of the various physical properties being considered, the most important characteristic of a sorbent for adsorptive purpose is its high porosity [6]. In a broader concept, sorbents are characterized for [3, 6]:

- Pore textural properties: include Specific Langmuir and Bruauer-Ennett-Teller (BET surface area), pore volume, pore size distribution
- Adsorption capacity
- Bulk density
- Crushing strength (structural stability)
- Crystal phase structure: via XRD (X-ray Diffraction)
- Thermal stability: could be done by using a Thermogravimetric analyzer (TGA)
- Surface morphology and crystal particle size: via Scanning Electron Microscope (SEM)
- Sorbent cost
- Reaction rate and
- Cycle time

Furthermore, sorbents from carbonaceous materials [12] such as activated carbon, biochar etc. are classified based on:

- Volatile matter
- Fixed carbon and
- Ash content

These properties are measured according to ASTM D1762-84 (ASTM-2007) and are called proximate analysis.

2.2 Types of Sorbents

For adsorptive purposes, literature reveals various kinds of industrial sorbents as followings.

2.2.1 Activated Carbon

The raw material for the production of activated carbon are carbonaceous materials such as peat, wood, coals, petroleum coke, coconut shell [6] etc. The following basic steps are involved in the modern manufacture of this sorbent, including:

- Preparation of the raw material
- Pelletizing
- Low-temperature carbonization and
- Activation

In contrast to other major sorbents, the unique surface property of activated carbon is its non-polar or slightly polar surface which is as a result of the surface oxide groups and inorganic impurities. This unique property gives activated carbon the following advantages:

- Processes requiring separation and purification without prior stringent moisture removal.
- It adsorbs more non-polar and weakly polar organic material than any other sorbent due to its large accessible internal structure [6].
- Lower heat of adsorption or bond strength than any other sorbent [6].

2.2.2 Molecular-sieve Carbon

Molecular-sieve carbon can be employed in separation processes involving wet-gas stream and they are less hydrophilic than zeolite [6]. It is largely applied in the production of nitrogen from air.

2.2.3 Activated Alumina

Activated alumina has one of the greatest affinities for water. Industrially, it is an important sorbent applied for drying of gases and liquids, because of its hydrophilic property and large surface area. It also finds an important application in chromatography and in drying hydrocarbons produced by thermal cracking of petroleum fractions. With prolong use; it suffers loss of adsorption capacity due to coking and contamination.

2.2.4 Silica Gel

Silica gel is a rigid continuous network of spherical particles of colloidal silica, which is one of the synthetic amorphous silica. Commercially it is prepared by mixing sodium silicate solution with mineral acids such as a hydrogen tetraoxosulphate VI or hydrochloric acid. As a result of its high surface area and unique surface properties, silica gel is a desirable sorbent for drying [6].

2.2.5 Zeolite

Zeolites are natural or synthetic crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium, and calcium [6]. Commercial zeolite pellets are produced in the following sequence:

- Synthesis i. e gel formation between sodium hydroxide, sodium silicate and sodium aluminate in aqueous solution at room temperature.
- Pelletizing and
- Calcination

Some important applications of zeolite in gas separation process are air separations for the production of nitrogen and oxygen, hydrogen purification, recovery of n-paraffins from branched-chain and cyclic hydrocarbons, aromatic hydrocarbon separation and drying [11].

2.2.6 Metal Organic Frameworks (MOFs)

Metal Organic Frameworks are crystalline compounds consisting of metal ions and clusters coordinated in rigid organic molecules forming one, two and three dimensional porous structures [2]. According to DOE/NETL report [2], they represent a class of porous materials offering several advantages for CO_2 capture due to their ordered structure, high thermal stability, adjustable chemical functionality that can be manipulated by modifying the metal group or organic linker [2, 9, 10], extra-high porosity, and availability of hundreds of crystalline, well-characterized porous structures.

MIL-101(an acronym for Material Institute Lavoisier) is one of the most promising MOFs for gas capture due to its large surface area and pore volume, especially its stability upon water adsorption [13, 14].

2.2.7 Biochar

According to the advisory committee of the International Biochar Initiative, biochar is a fine grained charcoal high in organic carbon and largely resistant to decomposition. The production of biochar is through the pyrolysis of plant materials and waste feedstock. Literature shows various important application of biochar, which includes:

1. Soil amendment due to its highly porous structure thus having the following soil restoration properties [14]

- Improvement of chemical and physical properties of the soil
- Improve fertility for crop establishment
- Increase biomass productivity
- Increase water holding capacity
- Increase pH, electrical conductivity and cation exchange capacity
- Increase population of phosphate solubilizing and nitrogen-fixing bacteria
- Decrease bulk density and
- Increase percentage of 1-2mm water stable aggregates

2. Carbon stabilization and sequestration (carbon sink): apart from its major role as carbon sink, biochar also prevents N_2O and CH_4 releasing from the soil [11].

Bagreev and Hitoshi [15, 16] reported the heterogeneous nature of the biochar surface, with complex defect structure and significant quantity of organic and metallic compounds, see Figure 2-1. It showed that N_2O, CO_2 and methane can also be adsorbed on the highly porous surface of biochar.

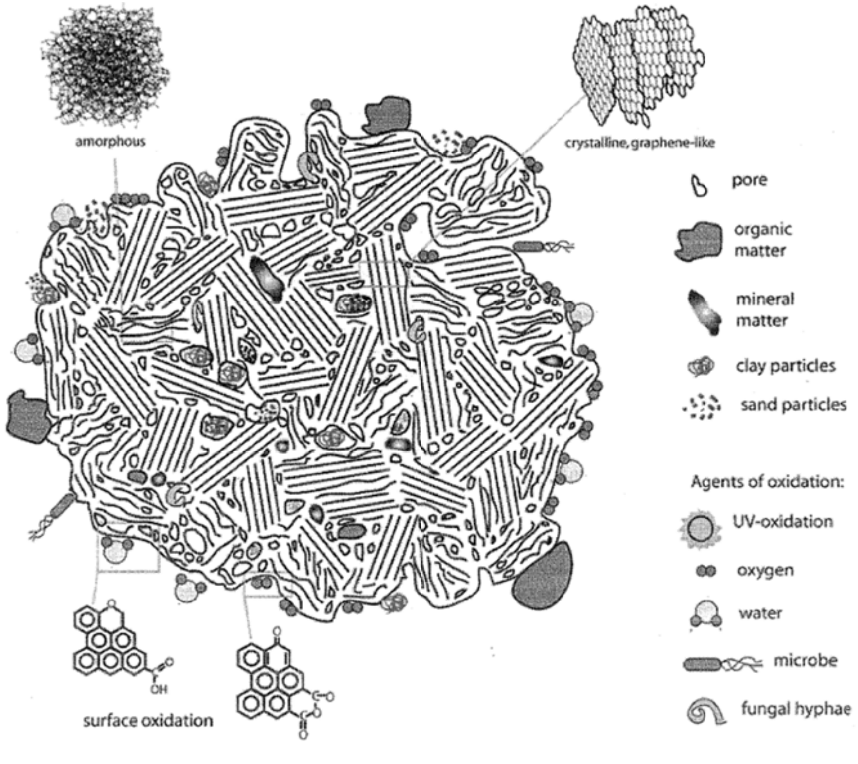


Figure 2-1: A Basic Model of a Complex Biochar Particle in the Soil [a] [11]

Note: Surface oxidation via various agents and the adsorption of organic matter from the soil characterizes a very important property of biochar [11]. Biochar's most important surface oxidation products are shown in the figure above include phenol, carbonyl and carboxylic acid groups [11].

[a] According to Lehmann, this biochar model consists of "two main distinguished structures, crystalline graphene-like sheets surrounded by randomly ordered amorphous aromatic structures and pores of various sizes" [11].

2.3 Configurations for CO_2 Capture

The DOE-NERL's CO_2 capture research and development covers a wide variety of advanced CO_2 capture technologies, namely:

- Pre-combustion CO_2 capture
- Post-combustion CO_2 capture
- Oxy-combustion CO_2 capture
- Chemical-looping

2.3.1 Pre-combustion CO_2 Capture

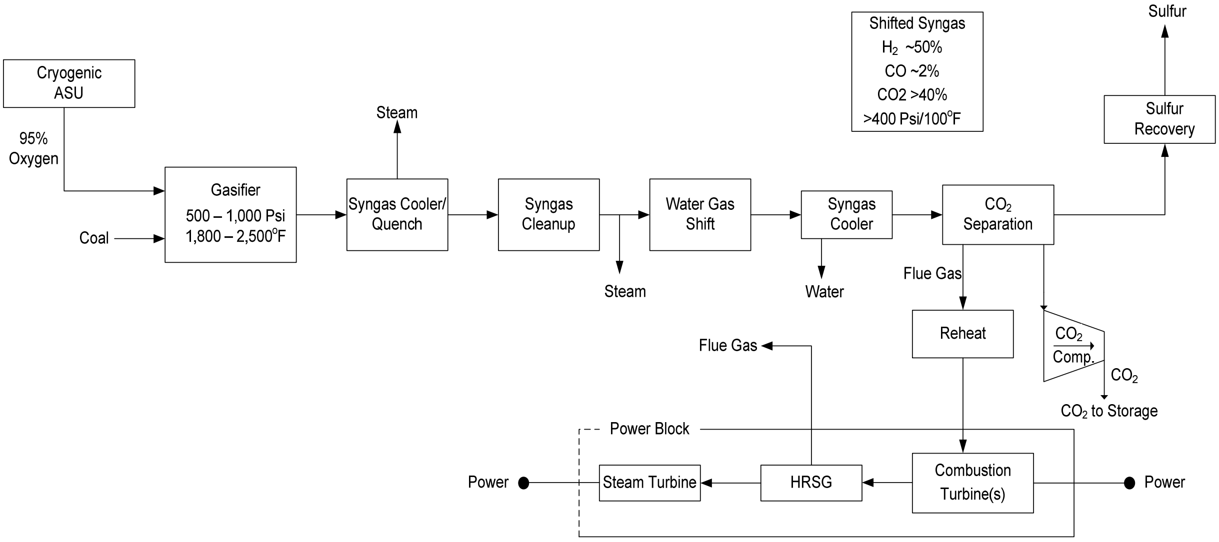


Figure 2-2: Block Diagram of Pre-Combustion System [2]

In gasification plants, fuel is converted into syngas (H_2 and CO), along with minor amount of other gases (see Figure 2-2). After CO is processed to produce H_2 in a water-gas shift (WGS) reactor, the other product CO_2 should be removed from the syngas, which is at a higher pressure compared to the flue gas. The CO_2 removal should be easier and less cost for pre-combustion than for post combustion [2].

2.3.2 Post-combustion CO_2 Capture

CO_2 capture is for the flue gas from combustion before emitted into the air. This process is the downstream of the conventional pollutant controls (see Figure 2-3), which is challenging because the flue gas to be treated is at low pressure (15-25 psi), and it has a relatively large volume with a low concentration of CO_2 (13-15 vol% in coal-fired power plants, 3-4 vol% in gas-fired turbines), and trace impurities (particulate matter, sulfur oxides, nitrogen oxides, etc.) [2].

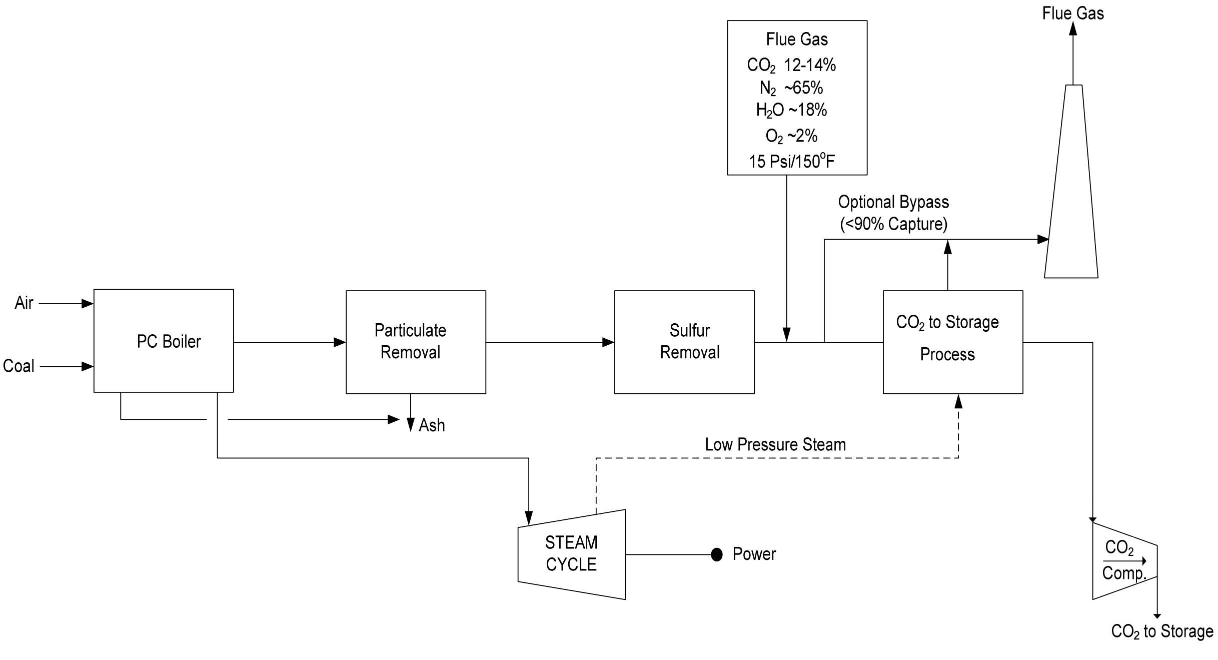


Figure 2-3: Block Diagram of Post-Combustion System [2]

2.3.3 Oxy-combustion CO_2 Capture

With flue gas (CO_2 or CO_2/steam) recycle, coal is burnt with relatively pure O_2 (>95%). By condensing H_2O vapor through cooling and compression, CO_2 is separated from the flue gas (see Figure 2-4). Because the partial pressure of CO_2 is ~60% in the flue gas, it is much easier and costs less for the CO_2 purification and compression process than a conventional post-combustion capture system [2].

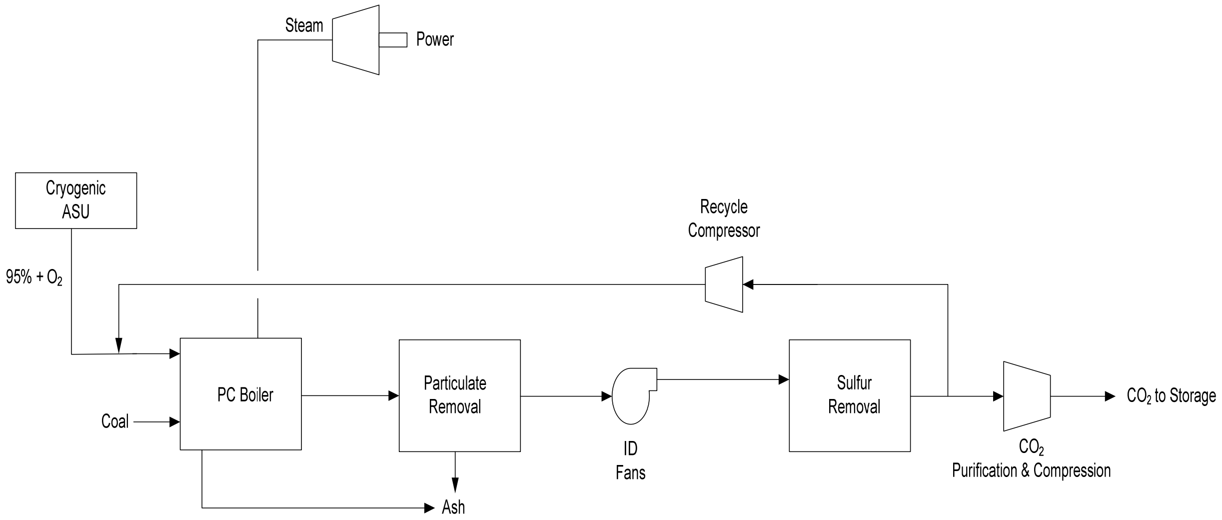


Figure 2-4: Block Diagram of Oxy-Combustion System [2]

2.3.4 Chemical looping

Chemical-looping combustion (CLC) thermal cycle has been proposed, combining chemical energy release with CO_2 recovery, which can highly utilize chemical energy of fuels and pay no energy penalty for CO_2 recovery simultaneously **[100]**.

Figure 2-5 illustrates CO_2 recovery in CLC. It consists of two reactors: a reduction reactor (or fuel reactor) and an oxidation reactor (or air reactor). The novel combustion manner decomposes traditional combustion of fuel into two-step reactions, using CH_4 as fuel.

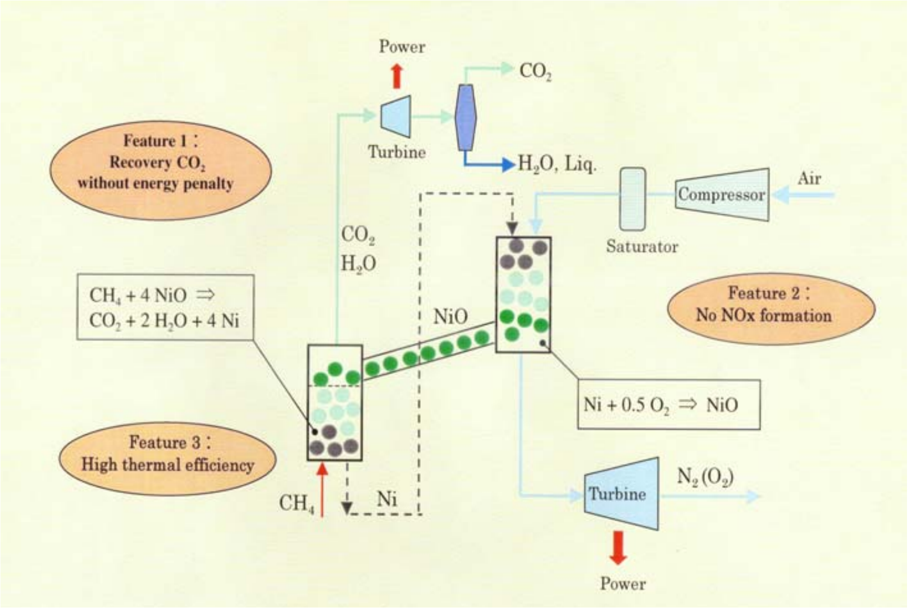


Figure 2-5: Concept Diagram of a Gas Turbine Cycle with Chemical-looping Combustion [100]

CLC achieves the integration of chemical energy release from fuel and CO_2 recovery. In this process [100], reactions of fuel gas and air with solid materials are carried out in separated reactors. Thus, CO_2 from reduction reactor does not mix with nitrogen, and its concentration is much higher than that in the case of conventional combustor. It becomes easy for CO_2 capture by condensing vapor into water. So CLC system does not require CO_2 separation device, which means that it has the characteristic of inherent CO_2 recovery without additional energy consumption. The temperature of non-flame reaction is much lower than general combustion temperature, which could make great contribution to completely eliminating another greenhouse gas NO_X (not just reduced to some extent).

2.4 CO_2 Capture R&D Programs

With coal-fired power plants contributing about 40 percent of anthrogenic CO_2 emitted into the atmosphere [7], clean coal research programs aiming at either reducing or eliminating the emission by cost-effective CO_2 capture technologies become of great energy, environmental and economic interest. Clean Coal Research program currently comprises of nine distinct areas [2] namely:

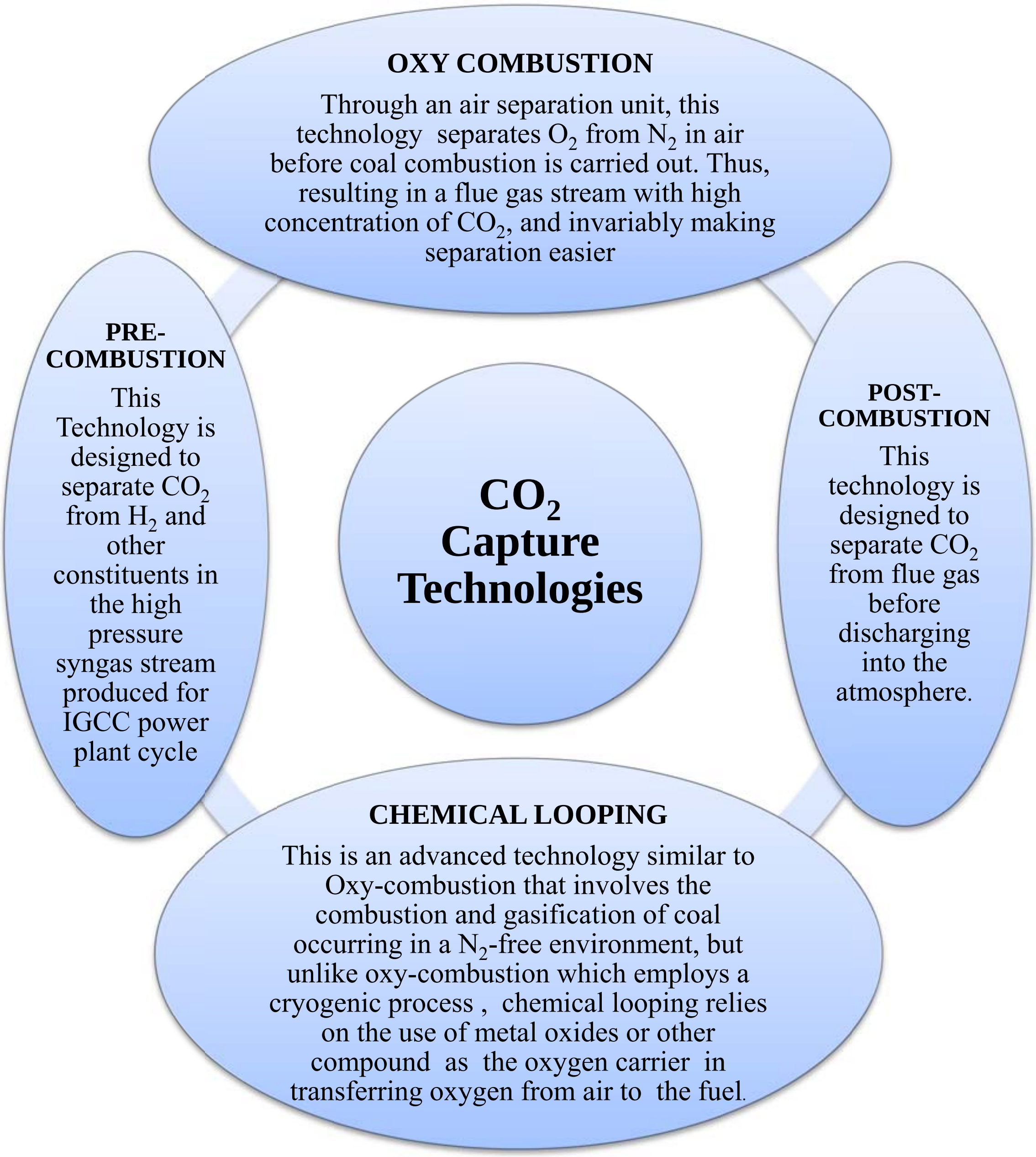
- Innovations for Existing Plants (IEP)
- Advanced Turbines
- Advanced Integrated Gasification Combined Cycle (IGCC)
- Carbon Sequestration (CS)
- Solid State Energy Conversion Alliance (SECA) Fuel Cells
- Fuels
- FutureGen
- CCPI and
- Advanced Research (AR)

The IEP program area basically focuses on developing post-combustion, oxy-combustion and advanced compression technologies applicable to new and existing pulverized coal (PC) power plants [2].

The Carbon Sequestration program area plays a leading role in pre-combustion CO_2 emissions control for IGCC power plants and also focuses on the development of CO_2 storage technologies in geological sequestration and its associated monitoring, verification and accounting [2]. Additional research and development in pre-combustion CO_2 capture technologies are done in the IGCC and Fuels program areas, while the Membrane-based systems for the separation of H_2 and CO_2 in coal derived syngas is the major focus of the Fuels program area [2].

2.5 Basic Scientific Principles and Important CO_2 Capture Technologies

DOE-NETL [2] approaches CO_2 capture in three ways. Figure 2-6 below gives a summary of the four technological approaches.



OXY COMBUSTION

Through an air separation unit, this technology separates O_2 from N_2 in air before coal combustion is carried out. Thus, resulting in a flue gas stream with high concentration of CO_2, and invariably making separation easier

PRE-COMBUSTION

This Technology is designed to separate CO_2 from H_2 and other constituents in the high pressure syngas stream produced for IGCC power plant cycle

CO_2 Capture Technologies

POST-COMBUSTION

This technology is designed to separate CO_2 from flue gas before discharging into the atmosphere.

CHEMICAL LOOPING

This is an advanced technology similar to Oxy-combustion that involves the combustion and gasification of coal occurring in a N_2-free environment, but unlike oxy-combustion which employs a cryogenic process , chemical looping relies on the use of metal oxides or other compound as the oxygen carrier in transferring oxygen from air to the fuel.

Figure 2-6: CO_2 Capture Technologies

2.6 Operational Processes for CO_2 Capture

The basic scientific principles [2] of the four major CO_2 capture technologies can be approached in the following ways namely:

- The sorbent based process
- The solvent based process
- The membrane based process
- The low temperature of cryogenic process and
- The oxy-combustion process

The focus of this review is on the sorbent based process.

2.6.1 The Sorbent Based Process

In the cryogenic separation of air into nitrogen and oxygen, at least CO_2 and water have to be removed from the feed gas to form a pure gas for subsequent separation by cryogenic treatment. The removal of CO_2 and water as well as trace amount of hydrocarbon such as acetylene from the feed gas prior to the cryogenic separation of oxygen and nitrogen is necessary to:

- Prevent the freezing of CO_2 and water vapor which may interfere with the subsequent cryogenic treatment and
- Prevent the risk of explosion due to possible accumulation of hydrocarbons such as acetylene during the cryogenic treatment.

Three methods generally used in separating CO_2 and water from a feed gas by adsorption onto a sorbent are:

- Pressure swing adsorption
- Temperature swing adsorption and
- Electric swing adsorption

2.6.1.1 Pressure Swing Adsorption (PSA)

The pressure swing adsorption is a technology used in separating some gaseous species from a mixture of gas under pressure. It can be achieved by taking advantage of the species molecular characteristics and affinity for the adsorbent material. Unlike cryogenic distillation techniques of gas separation, PSA is operated at near ambient temperature [19].

Yang [6] reported the existence of a multitude of sophisticated PSA processes and design which are being implemented for various separations. The performance of the PSA separation process is a measure of three quantities name:

- Product purity: which is the volume-average quantity of the effluent concentration and flow rate from the PSA process,
- Product recovery: which is a measure of the amount of component that is contained in the product stream divided by the amount of the same component in the feed stream, and
- Adsorbent productivity: is a measure of the amount of the product to feed mixture processed per unit amount of sorbent per unit time.

For any given separation, the product purity is predetermined, the energy requirement is usually proportional to the recovery, and the size of the sorbent bed is inversely proportional to the sorbent productivity [6].

The pressure swing adsorption processes rely on the fact that under pressure, gases tend to be attracted towards the solid surfaces i.e. they tend to be adsorbed. More gas is adsorbed on the solid surface at a higher pressure and on a reduction in pressure the adsorbed gas is desorbed. Thus, the PSA process can be used to separate gases in a mixture because different gases tend to be attracted to different solid surfaces either more or less strongly.

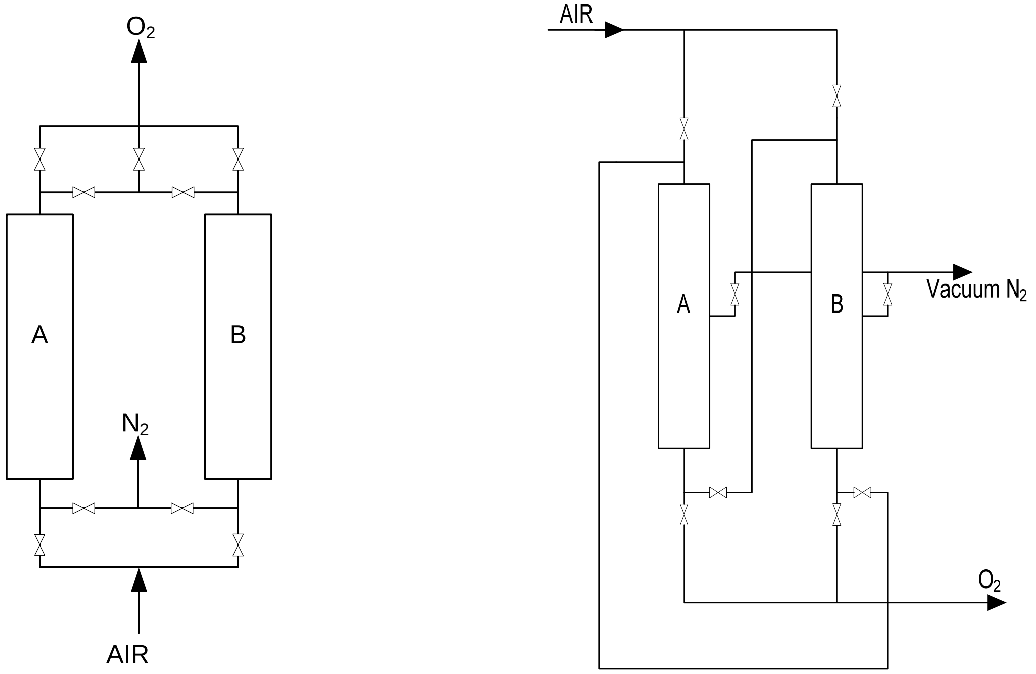
Figures 2-7 (a) and (b) gives a summary of two basic PSA cycles, i.e. the Skarstrom cycle and the Guerin-Domine cycle.

The Skartrom cycle also referred to as heatless adsorption with original patent filed in 1958 by Esso Research and Engineering Company [17], after the adsorption step the first bed is depressurized to atmospheric pressure and at the same time, the compressed feed mixture is switched to the second bed to repressurize it. Thus the adsorption step starts at the feed pressure, with a fraction of the purified effluent from the second bed passed through the second bed in a countercurrent direction to the feed direction, so as to purge the bed at atmospheric pressure. After this purge the unit is ready for the next cycle, with each bed undergoing two half cycles at equal times.

For a purification process, steady and continuous flows of both feed and purified products are achieved.

The Guerin-Domine cycle [18] is a versatile one that depends on the nature of the mixture to be separated. It varies in the number of beds, interconnections, and operational scheme. Designs of one to six beds have been proposed [18]. Figure 2-7 (b) is a two-bed model, with each bed going through three steps:

- Pressurization, i.e. with only the feed end open
- Depressurization, i.e. through the other beds, both a concurrent direction with the feed when oxygen is formed, and
- Evacuation from the midpoint of the bed when nitrogen is withdrawn.



(a) Skarstrom Cycle[17]

(b) Guerin-Domine Cycle[18]

Figure 2-7: Schematic of Two Basic PSA Cycles

One technical advantage of pre-combustion sorbent technology is that CO_2 can be recovered via pressure swing adsorption.

2.6.1.2 Temperature Swing Adsorption (TSA)

Like the pressure swing adsorption the temperature swing adsorption is also a technology employed in separating some gaseous species from a mixture of gas under pressure. This is also achieved by taking advantage of the species molecular characteristics and affinity for the adsorbent material. Like PSA, in TSA the bed is exposed to the feed gas for a period for the gases of interest to be adsorbed, but unlike PSA, TSA requires heat to be supplied for the adsorbed gas to be desorbed from the sorbent during the regeneration phase and this heat is supplied by the heated generating.

In the TSA process, the adsorption phase is carried out over a prolonged period and the liberated heat of adsorption of the adsorbate on the sorbent is displaced out of the bed by the flowing gas. It is also necessary that the adsorbent bed has substantial capacity for adsorbing the adsorbate of interest [19].

Kalbassi et al reported that in the removal of CO_2 and water vapor in air prior to cryogenic air separation process, the common practice is to use molecular sieve sorbents such as zeolite 13X for both TSA and PSA [19, 20]. According to the report, the temperature difference between the regenerating gas and the adsorption should not exceed $50^{o}C$ and can be substantially less provided the flow of the regenerating gas is sufficient in providing the heat of desorption required [19].

Furthermore, in his report, Kalbassi stated that the TSA invention is preferably applied towards the removal of water and CO_2 from feed gas streams in which the CO_2 concentration is present at a low level such as 400ppm prior to the adsorption process [19].

Table 2-1 below presents a summary of the preferred process conditions for operating TSA. The regenerating gas should be fed to the adsorbent bed at a temperature which exceeds the temperature of the feed gas. The regenerating gas is preferable fed at temperature between 30^{o}C to 150^{o}C and at a pressure range between 0.5 to 0.8bara. This is not more than 50 percent of the pressure at which the feed gas is supplied. More preferably the regenerating gas is fed to the adsorbent at pressure from 1 to 3bara [19].

Table 2-1: Optimum Operating Condition for TSA [19]

Item	Range of operation	Preferred range
Feed gas supply pressure (bara)	2 - 20	2 - 15
Feed gas supply temperature (^{o}C)	5 - 50	10 - 40
Ratio of molar flow rate of regenerating gas to feed gas	0.1 - 0.8	0.2 - 0.5
Duration of feed gas to adsorbent prior to regeneration (min)	60 - 600	70 - 300 [a]

[a] Though the generally preferred range is 30 to 300mins, The most advantageous time period depends on the size of the adsorbent bed used.

Note: however, the system could be designed with the regenerating gas pressure higher than the feed gas pressure provided the purge to feed ratio and the purge temperature are high enough [19].

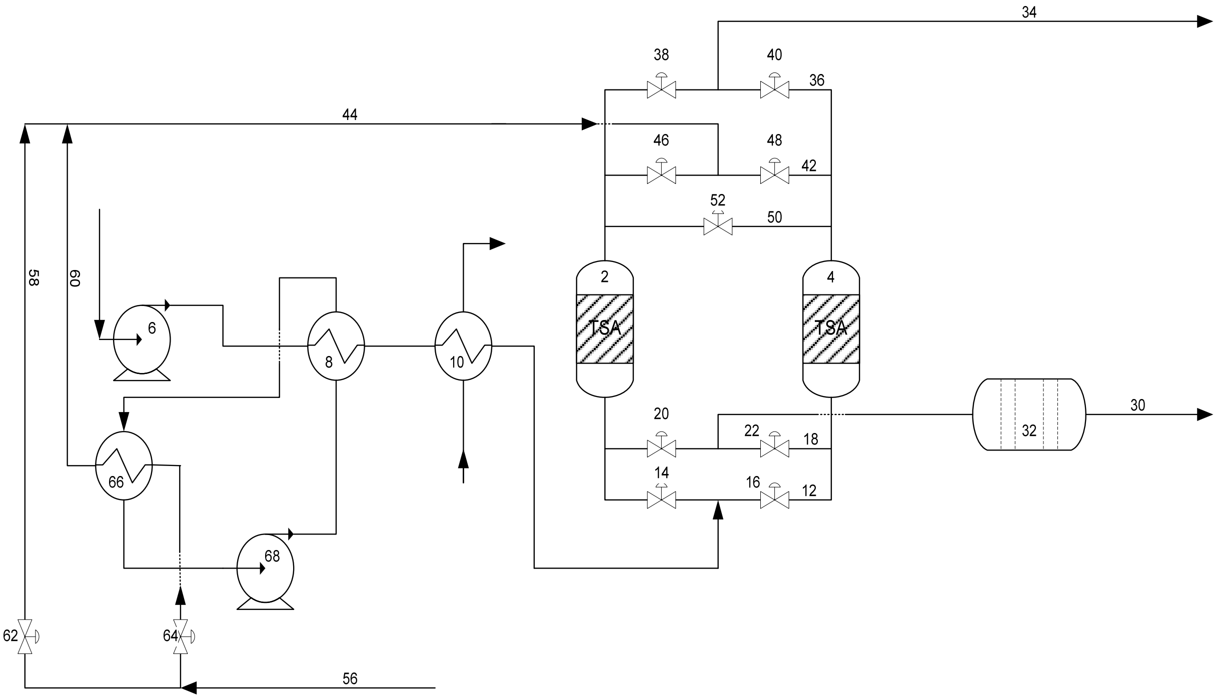


Figure 2-8: Schematic of a TSA Cycle [19]

Figure 2-8 above shows a schematic of the TSA comprising of the followings:

1. At least two pairs of adsorbent beds containing columns or vessels.
2. Purified air supplied by air compressor 6.
3. Heat exchanger 8 and 10 for removing heat produced during air compression.
4. The compressed air is supplied to the inlet manifold 12 containing control valves 14 and 16 to which is connected the pair of adsorbent bed containing columns 2 and 4.
5. The inlet manifold is bridged downstream of the control valve 14 and 16 by a venting and depressurizing manifold 18 containing valves 20 and 22 which serve to close and open connection between the upstream ends of respective adsorbent column 2 and 4 and a vent line 30 fitted with a silencer 32.

6. 34 is the outlet for the purified gas connected to the downstream ends of the two adsorbent columns 2 and 4 by an outlet manifold 36 containing control valves 38 and 40 upstream of which the outlet manifold 36 is bridged by a regenerating gas manifold 42 connected to line 44 supplying the regenerating gas and containing valves 46, 48 by which the flow of the regenerating gas may be connected selectively to either of the adsorbent containing columns 2, 4.
7. The manifold 50 containing control valve 52 bridges the downstream ends of the columns 2, 4 for the purpose of repressurization.
8. The produced purified gas is supplied to the cold box of an air separation unit which separates air into oxygen and nitrogen. Dry CO_2 free gas from the cold box supplied to an inlet 56 which is connected to the inlet of the regenerating gas 44 via two selectable paths 58 and 60 controlled by respective control valves 62 and 64.
9. Line 58 leads the regenerating gas directly to the regenerating gas inlet 44 while line 60 leads through the heat exchanger 66 which supplies heat to the regenerating gas through water circulated by pump 68 through heat exchanger 8 and 66.
10. Heat exchanger 10 has a cold water inlet and outlet for controlling the temperature of the supplied feed gas.

For flue gas with low CO_2 content, Ishibashi et al. [22] reported the use of combined temperature and VPSA (Vacuum Pressure Swing Adsorption). Merel et al. [25] proposed the use of TSA. The main inconvenience of the TSA process is the long time for desorption cycles that can be reduced by maximizing the contact area of the hot gas and the adsorbent [25, 27].

2.6.1.3 Electric Swing Adsorption

The electric swing adsorption is a process that can increase the temperature of the adsorbent at a very fast rate [21]. In this, a low voltage electric current is employed to heat the adsorbent by the direct joule effect [23]. One disadvantage of the ESA compared to the TSA is that temperature increase is achieved by using electric power while waste heat is employed for the TSA.

In a natural gas combined cycle (NGCC) plant, for the CO_2 produced and due to the complex energetic integration already implemented, the amount of waste heat may not be enough to be employed in a TSA process as a result, the ESA may be an interesting alternative [24, 28, 29] reported as a case of TSA and ESA comparison for the recovery of volatile organic compounds that could be removed by ESA process with much higher unit productivity. Desorption of CO_2 from flue gas with ESA was proposed by Ettlili et al. [26] by employing an indirect heating system for the bed filled with zeolite 13X.

Grande et al. [21] in the study of the operation of ESA process in the capture of CO_2 from natural gas combined cycle power station with low CO_2 concentration in the feed stream reported the use of activated carbon honeycomb monolith with low electrical resistivity as a selective adsorbent. Figure 2-9 below is a schematic diagram of the set up employed for the measurement on the adsorption and desorption breakthrough curve for an ESA cycle.

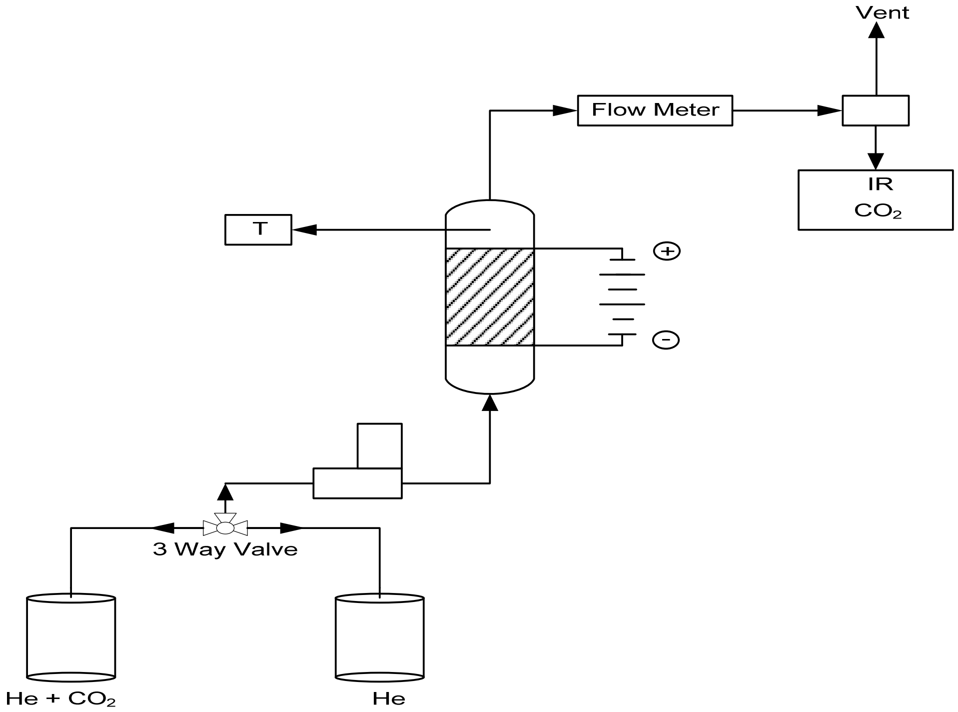


Figure 2-9: Schematic of ESA [21]

2.6.2 Amine Based Adsorption (Solvent Based)

Solvent based CO_2 capture generally involves CO_2 absorption either chemically or physically from combustion flue gas or other sources into a liquid carrier [2]. The absorption liquid is regenerated by increasing its temperature or reducing its pressure. The development of low cost, non-corrosive solvents with high CO_2 loading capacity, low regeneration energy, improved reaction kinetics and resistance to degradation defines the goal of DOE/NETL's current research and development objectives [2].

Generally, amines and ammonia based solvents are used for CO_2 capture. Figure 2-10 below shows a schematic diagram of a MEA process [2].

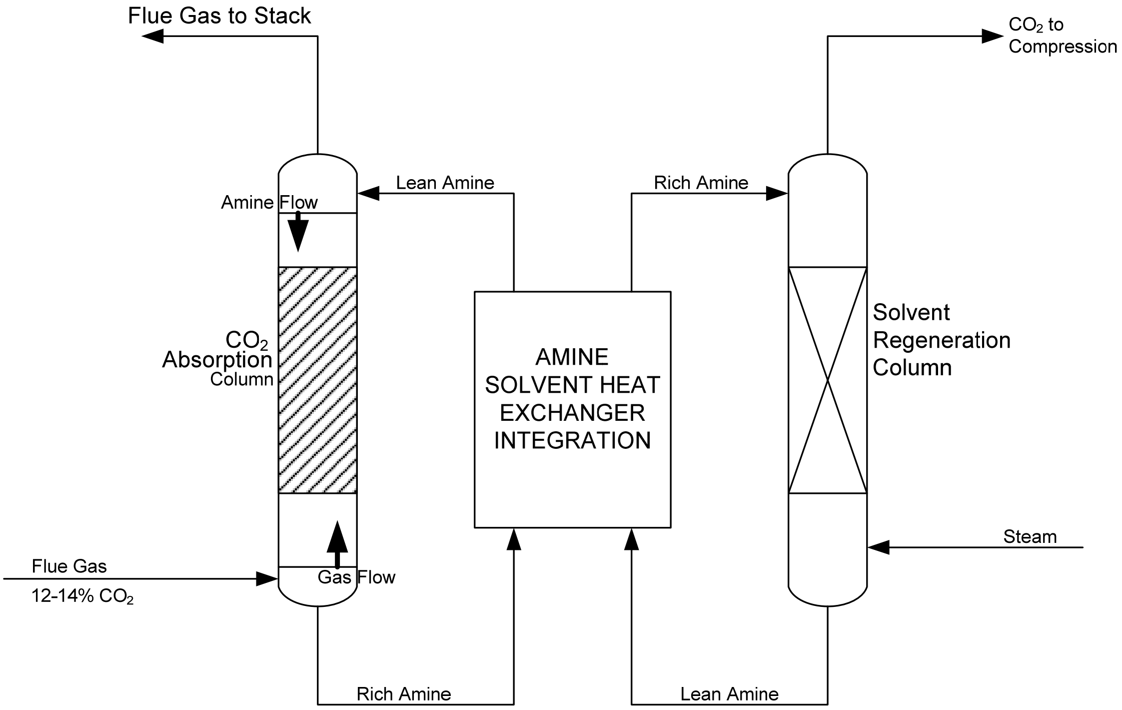


Figure 2-10: Schematic Diagram of Post-combustion MEA CO_2 Capture Process [2]

In this figure, the combustion flue gas enters an absorber reactor and flows counter-currently to a CO_2-lean MEA solution where CO_2 is absorbed into, and chemically reacts with MEA. Nitrogen gas being the primary component of the treated flue gas is discharged to the atmosphere while the CO_2-rich solution is pumped to a stripper reactor for regeneration.

In the stripper, the solution rich in CO_2 is heated in order to reverse the amine- CO_2 chemical reaction thus, stripping the CO_2 out of solution. The reboiler, supplied with extraction steam from the turbine cycle, provides the heat for regeneration of the MEA solvent in the stripper. Consequently, CO_2 is released, producing a concentrated stream which exits the stripper and is then cooled and dehumidified in preparation for compression, transport, and storage. The CO_2-lean solution from the stripper is cooled and returned to the absorber for reuse.

The amine solvents currently used are corrosive and susceptible to degradation by trace flue gas constituents (particularly SO_X); thereby necessitating significant amounts of energy, in the form of low-pressure steam, for sensible heating, heat of reaction, and stripping for CO_2 regeneration. According to the DOE report [2], installing the current state-of-the-art MEA post-combustion CO_2 capture technology on new conventional PC power plants would increase the COE by about 75 percent. Furthermore, the large quantity of energy required in regenerating the MEA solvent would reduce the net efficiency by approximately ten percentage points [2].

In addition to amines, ammonia-based solvents can be used for CO_2 capture. Ammonia based solvents rely upon temperature swing cycle between ammonia carbonate and ammonia bicarbonate. This reaction has a significantly lower heat of reaction than amine based systems, thus resulting in energy savings, provided the absorption/desorption cycle can be limited to this mechanism [2].

Ammonia-based absorption has a number of advantages over amine-based systems, such as the potential for high CO_2 capacity, lack of degradation during absorption/regeneration, tolerance to O_2 in the flue gas, low cost, and potential for regeneration at high pressure [2].

2.6.3 Membrane Based Separation

Membrane-based post-combustion CO_2 capture process involves the use of permeable or semi-permeable materials that allow for the selective separation of CO_2 from flue gas.

Membranes are more advantageous for separating CO_2 in high-pressure applications, such as coal gasification [2].

DOE/NETL focus on membrane based separation is on developing highly-selective and permeable membrane systems designed specifically for CO_2 separation from low partial pressure, post-combustion flue gas streams. Potentially, membranes could be a more cost-effective technology option for post-combustion CO_2 capture than solvents or sorbents that require a large amount of regeneration energy to separate CO_2. Membranes constructed of polymeric materials are currently being used in a number of industrial gas separation processes including air separation; hydrogen recovery from ammonia; dehydration of air; and CO_2 separation from natural gas. In general, membrane processes offer several potential advantages compared to other post-combustion CO_2 capture technologies including [2]:

1. Simple passive operation with no moving parts,
2. Immunity to chemical contaminants,
3. Energy-efficient with low operating costs, and
4. A small footprint that is easily expandable due to modular design components.

2.7 Operational Parameters for CO_2 Capture

Operational parameters that effect the sorbent materials application on post-combustion CO_2 adsorption include, but are not limited to, sorbent properties, sorbent cost, operation conditions of adsorption (i.e. temperature and pressure), sorbent regeneration, and contaminants in the flue gas.

Sorbent properties include the mechanical/thermal/chemical stability, surface area, particle size, CO_2 adsorption capacity, and heat of adsorption etc. These properties will impact the design and cost of an adsorption process. Adsorption capacity, heat of adsorption and sorbent regeneration will impact energy consumption. Major factors that influence the performance and cost of a sorbent are listed below. A summary of process parameters of different sorbents is shown in Table 2-2.

1. Surface Area

It is the exposed area on the surface of the sorbent which can adsorb gas. The more adsorption can take place per unit sorbent if a sorbent has larger surface area. It is desirable for sorbents to be porous so as to maximize adsorption with the smallest amount of sorbent resulting in lower sorbent costs and lower process equipment costs. Reported values vary between 0.5 - 1,500 m^2/gram of sorbent [2].

2. Pore volume

Pore volume is defined as the ratio of the void spaces in a porous material to the total volume of a porous material. Its value is between 0-1.

Surface area and pore volume of the sorbents can be measured by BET, and Langmuir methods etc.

3. Selectivity

The ability of a sorbent to separate a gas from other gases is measured as the selectivity, which is the ratio of the individual gas permeability or permeance. Sorbent selectivity and pressure ratio determine CO_2 purity.

4. Thermogravimetric analysis

Thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines the relation of weight change based on temperature change. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. It can characterize thermal stability of a sorbent. Various literatures have reported the use of TGA in isothermal measurements of sorption studies. Huang et al. [31] reported the adsorption of CO_2 and H_2S on amine modified silica xerogel and MCM-48 supports. In this report [31], a rapid weight gain was observed in the uptake of CO_2 on 3-aminopropyl functionalized MCM-48 sample. At 80% completion, the amount of CO_2 adsorbed at room temperature was 50mg/g of sorbent and this was accomplished in the first 30 minutes. Under similar conditions, the reported uptake of CO_2 on unmodified MCM-48 sample was 14mg/g of sorbent. Thus indicating a stronger affinity for CO_2 for the amine modified MCM-48 surface, which is as a result of a weak chemical interaction between the basic amine groups and CO_2. The TGA results reported by Huang et al., shows the thermal reversibility of the adsorption-desorption reaction of CO_2 on the amine modified surface.

5. Chemical structure

The chemical structure of the sorbents can be determined by the following common methods:

- X-ray diffraction (XRD)
- Proton NMR
- Carbon-13 NMR
- Mass spectrometry
- Infrared spectroscopy

6. Adsorption capacity

Adsorption capacity, which is the CO_2 loading difference between the inlet flue gas and outlet gas passing through the sorbent, will influence the required sorbent amount of the process and equipment size. If TSA is used for regeneration, then the energy consumption will also be affected. A higher adsorption capacity is always beneficial on a basis of other sorbent properties being the same. Adsorption capacity can be measured by how much CO_2 is captured per gram of sorbent. Reported CO_2 adsorption capacity can achieve as high as 21 percent by weight [2].

7. Heat of adsorption

Heat of adsorption determines the energy demand during sorbent regeneration (i.e., desorption). A higher heat of adsorption means more energy required for regeneration. Heat of adsorption also impacts the regeneration mode of an adsorption process. Higher heat of adsorption also implies that the adsorption working capacity is more sensitive to the regeneration temperature (i.e., a small change in temperature will result in a great change in capacity, and thus TSA regeneration is more favorable). Typically a chemical sorbent uses a TSA regeneration design, while a physical sorbent uses PSA regeneration more. Reported values for heat of adsorption can range at 11.7 - 1760 kJ/mole [2].

8. Crush strength

The stress strength of the sorbent is important in a process, such as a fluidized bed. A physically weak sorbent undergoes attrition too quickly that can crush it to ineffective powder, which will cause more frequent replacement of the sorbent.

9. Cycle time

The cycle time of an adsorption process is vital for fixed-bed configurations, especially when the process scale is large. If the sorbent remains very long time in the adsorption reactor for a cycle, it will result in very little CO_2 being captured, more amount of sorbent, larger equipment size, and a larger plant area being needed, in spite of the sorbent has a very large CO_2 working capacity.

10. Number of expected cycles

It is expected that sorbents degrade over time, either through physical attrition or chemical degradation such as from sulfur or oxygen. It is desirable for a sorbent to be cycled for a great amount of times before replacement. The reported expectation of the cycles ranges at 1800 - 10000 before needing to be replaced [2].

11. Sorbent costs

A promising sorbent would be produced with a low cost and would be composed of materials that are readily available, i.e. a material that could be mined and put into service with minimal processing requirements.

12. Contaminant resistance

Flue gas contains various gases, i. e. CO_2, N_2, SO_2, and H_2O etc., which impact the CO_2 adsorption on the sorbents.

All favorable properties such as large surface area, low cost, short cycle times, and small swings between pressure and temperature should be exhibited in an ideal sorbent. However, it is not expected that any one sorbent can exhibit all of the best properties, which means economic analyses will be critical in the determination of which sorbent and which combination of properties will cost lowest for a particular plant. The total capture cost for each sorbent and associated process can come from a number of different factors and be greatly influenced by various properties of the sorbents, while the final aim is to capture CO_2 with minimal impact on COE.

2.8 Technical challenges for CO_2 capture technologies

The key technical challenges for CO_2 capture on coal-fired power plants include the application of presently available CO_2 capture technologies, energy integration, flue gas contaminants, water use, CO_2 compression, and oxygen supply for oxy-combustion systems.

2.8.1 Key technical challenges for CO_2 capture technologies

1. Scale-up

Current commercially available CO_2 separation processes have not been applied at large scale power plants, whose application could dramatically increase costs of electricity generation.

2. Cost-effectiveness

Present CO_2 capture technologies are expensive and energy-intensive according to NETL studies, which significantly degrade the overall energy efficiency of existing and future coal-based power plants. For instance, the levelized cost of energy (COE) of the current aqueous MEA solution chemical adsorption for post-combustion CO_2 capture is estimated to have an increase of about 75-80%.

3. Auxiliary power

To operate presently available increase capture technologies, it requires great quantity of auxiliary power, which reduces the net electricity production of the power plant.

4. Steam usage

The solvents or sorbents used for commercially available CO_2 capture technologies demand a significant amount of energy for regeneration (~3605 kJ/kg of CO_2 removal), which greatly decreases net power output.

5. Energy integration

Steam extraction from the power generation would be provided for the regeneration of the solvents or sorbents in commercially available CO_2 capture technologies, which brings out the requirement for efficient energy integration of the steam cycle to the CO_2 capture part in the power generation system.

6. Flue gas contaminants

Flue gas components other than CO_2 especially sulfur and water vapor can cause additional operational costs to remove.

7. Water use

CO_2 capture and compression cooling requires a lot of water use.

8. CO_2 compression

It requires large quantity of energy to compress the captured CO_2 to typical pipeline levels for sequestration (10-15 MPa relying on the scheme and location of CO_2 sequestration). It is essential to decrease this energy consumption to upgrade the overall plant energy efficiency and achieve CO_2 sequestration in present and new power generation systems.

9. Oxygen supply

High purity oxygen is required to supply for an oxy-combustion power plant, e.g. cryogenic air separation unit (ASU), a presently available technology, which is energy consumptive and cost intensive.

2.8.2 Technical advantages and challenges for sorbent-based CO_2 capture technologies

Both pre- and post-combustion CO_2 capture technologies could apply sorbent-based processes, whose technical advantages and challenges are summarized as following [2].

2.8.2.1 Pre-combustion Sorbent CO_2 Capture Technologies

1. Technical advantages

- CO_2 recovery is principally carried out on a basis of pressure swing (versus heat energy).

- H_2S usually has high solubility in the same sorbent as CO_2, which means both H_2S and CO_2 can be combined to remove from the flue gas.
- Some system concepts, like being recovered with some steam stripping instead of flashing, CO_2 could be delivered at an increased pressure, which is going to optimize the power system performance.

2. Technical challenges

- Loss of CO_2 pressure could happen during flash recovery.
- Syngas must be cooled for CO_2 recovery before being heated back up again and re-humidified for burning to turbine.
- Some loss of H_2 could present with CO_2.

2.8.2.2 Post-combustion sorbent CO_2 capture technologies

1. Technical advantages

- With large capacities and fast kinetics provided by chemical sites on the sorbents, it is able to capture CO_2 from flue gas at a low CO_2 partial pressure.
- The capacities on a unit mass or volume basis are higher than similar wet-scrubbing chemicals.
- It requires less heating compared to wet-scrubbing in many cases (depending on CO_2 and heat capacity).

2. Technical challenges

- Heat is required to regenerate the sorbent (although generally lower than in wet-scrubbing cases).
- When adsorption is an exothermal reaction, it is difficult to manage heat in a solid system, which can limit the capacity and/or cause operational problems.
- It could have a large pressure drop in flue gas applications.
- Sorbent attrition.

Table 2-2: Summary of Process Parameters for Different Sorbents

Type of sorbent	Sorbent properties										Mass tranfer coeff. (1/s)	Diffusion coeff. (cm^2/s)	Act. energy of CO_2 (kJ/mol)	Opertaing conditions						Ref.[h]
	Heat of ads. (kJ/mol CO_2)	CO_2 working capacity (mmol/g)	Surface area (m^2/g)	Pore vol. (cm^3/g)	Particle density (g/cm^3)	Packing density (g/cm^3)	Particle size (mm)	Heat capacity (kJ/K/kg)	Thermal stability (°C)	Hydro-thermal stability (°C)				Ads temp. (°C)	Ads. pressure (atm)	CO_2 capture eff. (%)	Regen.[g] method	Regen.[g] temp. (^{o}C)	Regen.[g] pressure (atm)	
Promoted MgO[e]	95-100	10-60	N/A		N/A	N/A	N/A	N/A	N/A	N/A				350-450	~24	>85	Thermal	500-550	~24	2
Activated Carbon[e]	N/A	9	1200		N/A	0.85		N/A		N/A				30	1	N/A	Electrical/ Thermal	N/A	N/A	2
Na_2O promoted Al_2O_3[e]	64.9	2.86	N/A		2.22	0.694	1.5	1.05	stale to 600^{o}C	Up to 550^{o}C				200-400	up to ~25	71	Thermal Swing	550	up to 40	2
Dry Sodium Carbonate[f]	3.08 MJ/kg[a]		100-120				0.065 - 0.075													2
Alkalized alumina[f]	12-25	0.16	100		0.63	1.05	1.6	0.8	650	110 - 650				110-200	1	90	Steam	100-200	1	2
MOF[f]	40-60	2.27-4.55	500-2000			0.3-0.7	0.5-2.0		250-400	100 - 200		8.1-11.5E-9[b]	7.61[b]	25-45	0.1-0.15	90-95	VPSA		0.01-0.05	2, 76-78
Carbon[f]	28	1.1364	1600		1.1	0.7	0.2	1	>400	>100				15-25	1	>95	direct steam	80-100	1	2
Supported amine, activated carbon[f]	~ -60	3-3.18	20-1500			0.3-0.7	0.03-0.1	1.4	100	not measured				55	1	100[c]	Temp. Swing	100	1[d]	2, 8
MIL-101[f,i]	4.0-28.6	3.62	2674-4230	1.3 - 2.30					<600		6.17E-4 - 38.1E-4	4.11E-11 - 2.54E-10	2.62 - 4.24	25	1					3, 12, 79-84
$AlPO_4$-14 Molecular Sieve		2												27	1					85
Zeolite 13X	49	2.2												25						86, 87
Amine-grafted SBA-15[j]	33 - 34	0.2-0.4																		44
TEPA/SiO_2[k]	3.2-11.0	2.087													1					88
PEG/TEPA/ SiO_2[f,l]	52	1.11-1.45					0.05 - 0.3	1.49	130					50			Temp. Swing	100-110	1 -1.05	2, 88

[a] Heat of adsorption.

[b] @295-331K (MOF-5).

[c] Laboratory scale.

[d] Laboratory scale total pressure.

[e] Pre-combustion sorbents.

[f] Post-combustion sorbents.

[g] Regeneration.

[h] Reference.

[i] MIL: acronym for Material Institute Lavoisier

[j] SBA-15: a mesoporous silicate

[k] TEPA: tetraethylenepentamine

[l] PEG: polyethylene glycol

3 THE CHEMISTRY OF GRAFTING – AMINE IMPREGNATION (REVIEW)

3.1 The chemistry of grafting – amine impregnation

3.1.1 General review

CO_2 capture and separation has been achieved via using solvents, membranes, cryogenic techniques and solid sorbents. When applied to CO_2 capture in dilute stream such as flue gas containing 15 vol.% of CO_2 for most coal combustion systems [30] or in acid gas sweeten process in nature gas production [31], large scale operations of these technologies could be capital intensive [30]. As a result, the development of highly efficient method for the removal of acid gas with lower economic cost becomes imperative.

Conventionally, sweetening of natural gas steam [32-36], or removal of CO_2 from flue gas stream from coal combustion plants is established by gas-liquid absorption i.e. stripping of the acid gas components of the gas stream by aqueous solutions of alkanolamines [32-36]. Commonly used amines include monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Despite the extensive application of current state of the art technology, the gas absorption process is not only highly energy intensive during solvent regeneration but also plagued with corrosion or degradation of the equipment through oxidation [31, 37, 38].

In enclosed habitable environment such as submarines and spacecraft [39-43] solid sorbents have been employed in the removal of CO_2 from the enclosed air. Though solid sorbent offers a number of advantages such as:

- Low energy requirement during regeneration [44]

- Elimination of problems associated with degradation or equipment corrosion due to oxidation [31, 37, 39, 45].

Their potential in terms of large scale applications such as CO_2 removal from flue gas of power plants and coal plant [46, 47] has not been fully exploited. Recent literature review [48-51] reveals that most sorbent studied for natural gas clean-up have at least one major problem that negates their industrial usage. For example zeolite and activated carbon which are most widely used as solid sorbent materials are limited because of the low selectivity of activated carbon toward acidic gases and the strong water inhibiting effect of zeolite materials.

Khatri et al. reported that "the cost of CO_2 capture can be drastically reduced if effective low-cost sorbents are designed that have a CO_2 adsorption capacity of more than 1000μmol/g of sorbent and a long-term regeneration capacity". In a similar angle, Chang et al. reported that "preliminary analysis has suggested that an economically feasible approach should cost less than \$10 to sequester a ton of CO_2 from stationary sources". They further stated that the "development of an economic CO_2 separation process requires a highly efficient CO_2 sorbent. The sorbent must possess high CO_2 capture and long-term regeneration capacity at the level above 2000μmol/g with a small difference in adsorption and desorption temperatures in the flue gas environment".

3.1.2 Silica substrate support

Several groups have reported the preparation on amine based silica sorbents from mesoporous amorphous silica gels [65], and mesoporous periodic framework structures such as SBA-15 [30, 44, 63], MCM-41[62], MCM-48 [31] and HMS [62].

The development of high surface area solid sorbents and catalysts has been of widespread interest. This may be connected to the fact that exceptionally high surface areas allow the binding to occur at a large number of highly dispersed active sites with the framework [52-61]. Huang et al. reported that silica and ordered mesoporous silica were ideal solid supports for the active functions because of their large surface area and pore volumes which are well defined. More significantly, the hydroxyl groups on the surface of the support are important for a number of surface phenomena, such as surface modification, gas adsorption, wetting etc. [89-92].

Huang et al. [31] reported the preparation of silica xerogel from tetraethoxysilane, ethanol, water, HCl and NH_4OH in the ratio of 1:3:1:0.0007 under constant reflux for 1.5 hours at 333K, with a surface area of $816 m^2/g$ after degassing at 200^oC, and MCM-48 obtained after 550^oC calcinations in air for 10 hours with a surface area of $1389 m^2/g$. According to Huang et al, the choice of silica xerogel or MCM-48 was due to their high surface areas and high surface densities of the surface –OH groups.

The preparation of mesoporous material SBA-15 using tetraethyl orthosilicate as the silica precursor was reported by Chang et al. [44], and Gray et al. [30]. In both papers, the procedures involved were well spelt out. The surface area of the SBA-15 support by Chang et al. was reported to be between 200-230 m^2/g, thus spelling the need for the surface area to be increased in order to bring it up to the level of economical CO_2 separation.

In line with the above findings, a large surface area, a well-defined pore structures and high surface densities of surface hydroxyl groups are important factors to be considered in the preparation of solid sorbent support [30, 31, 44]. Other examples of such solid supports include:

- Silica xerogel [31]
- PE-MCM-41 [62]

These supports are impregnated with primary, secondary or tertiary amine-based compounds. The idea of grafting the amine functionality onto the pore walls of the solid support is a known strategy for the design of promising new adsorbents and catalysts.

The general procedures employed in the preparation of a solid sorbent include:

- Substrate (solid precursor) preparation: this being the solid support and involves the use of a structural directing agent [63] (e.g. Pluronic 123), pore expander (e.g. 1,3,5-trimethylbenzene), and pH controller (e.g. HCl).
- Amination of the substrate: this involves the grafting of the substrate with primary, secondary or tertiary amine.

For obvious reasons, the use of solid sorbent could be a low cost alternative in the capture of CO_2 from power plant flue gas, natural gas stream because of its low heat capacity, high CO_2 adsorption capacity, and simplicity of operation. The total cost and utility cost could be used to determine the economic potential of the CO_2 capture process [66].

In terms of mass transfer limitation in comparing gas-sorbent interaction and gas-liquid interaction, the capture of CO_2 on solid sorbent involves direct adsorption of the gas on the solid surface of the sorbent which in this case could be the amine functional group on the surface. The rate limiting step for adsorption on solid sorbent is the diffusion of the gas (CO_2) from the bulk stream of the flue gas into the internal pore of the sorbent. For an aqueous amine process the rate limiting step is the mass transfer of CO_2 across the gas liquid interface [67]. The rate of the gas-solid mass transfer is usually three orders of magnitude higher than the gas-liquid interaction [68]. The higher mass transfer rate and adsorption capacity results in a smaller bed thus significantly minimizing construction and equipment cost [63].

3.2 Amine grafting process

One potential approach to sorbent preparation is grafting CO_2 adsorption sites on high surface area support [42,46, 47]. Recent research and development [52-61] shows a widespread interest in the development of high surface area solid sorbents and catalysts which would allow bonding to occur at a large number of highly active sites within the framework. This is achieved by exploiting the positive properties of gas-liquid adsorption through the grafting of the amine functional group on a mesoporous solid support [62].

The reason for the above research in developing energy and cost effective solid sorbent is due to the fact that the previous sorbents were designed for low levels of CO_2 capture and separation and the eventual use of these sorbents will make power generation from either coal combustion [63] or natural gas facilities [31] prohibitively expensive.

In the preparation and characterization of APTS-SBA-15 sorbent, by Chang et al. the γ-(aminopropyl)triethoxysilane (APTS) was prepared by impregnating an APTS/toluene solution into SBA-15. In the surface modification of silica-xerogel or MCM-48, Huang et al. reported the immobilization of the amine functional group on the silica surface by refluxing 1.0g of silica (silica-xerogel or MCM-48) with 50.0ml of toluene and 5.0ml of 3-aminopropyltriethoxy-silane. The quantitative determination of the amine functionality on the surface was obtained by a combined DTGA and weight gain measurements. Coverage of 2.3 and 1.7 mmol of

–$CH_2CH_2CH_2NH_2$ per gram of sorbent were reported for MCM-48 and silica xerogel, respectively [31].

Stein [94] and Sayari [95] extensively examined the modification of periodic mesoporous silica surfaces. A review of literatures concerning grafting of amine on silica based support under dry conditions reveals that the most promising result was that of Huang et al. [31]. In using the common dry grafting technique, Huang et al. grafted 3-aminopropyltriethoxysilane on periodic mesoporous MCM-48 silica thus obtaining an amine loading of 2.30mmol/g on a basis of total adsorbent weight. On exposure to feed gas mixture of 5% CO_2 in nitrogen, the equilibrium adsorption capacity obtained was 1.14mmol/g which translates to about 50mg/g. For a 100% CO_2 flow at 1.0atm total pressure 2.05mmol/g adsorption capacity was determined. In this same work it was reported that the adsorption capacity of the sorbent doubled in the presence of water vapor.

In more recent publications, Knowles et al grafted 3-aminopropyltrimethoxysilane onto a hexagonal mesoporous silica support (HMS), obtaining 2.29mmol(N)/g loading. The corresponding adsorption capacity for a 90% CO_2/Argon gas feed at 20^oC was 1.59mmol/g. Compared to the result presented by Huang et al. [31], Knowles et al. [65] showed significantly lower adsorption capacity for a similar monoamine loading. When the grafting material was further challenged with a 30% of relative humidity (RH) humid stream of CO_2, the adsorption capacity decreased slightly.

Harlick et al [62] grafted dry TRI with PE-MCM-41 silica. Thus obtaining an amine loading of 5.98mmol(N)/g (1.99mmol(organic)/g) with a corresponding dry 5% CO_2/N_2 adsorption capacity of 1.41mmol/g (62mg/g). However, unlike the result presented by Huang et al. [31], the grafted triamine material did not exhibit a doubling CO_2 adsorption capacity in the presence of a moist feed of CO_2. Rather a modest 8% increase was exhibited.

Khatri et al. [63] studied the adsorption and desorption of CO_2 on diamine - grafted SBA-15 via infrared spectroscopy coupled with mass spectroscopy. In this report, a secondary amine (diamine) was grafted onto a SBA-15 surface via the reaction of [N-(2-aminoethyl)-3-aminopropyl] trimethoxysilane with the surface hydroxyl functional group. At 25^oC CO_2 was adsorbed on the diamine grafted SBA-15 surface as:

- Bidentate carbonate
- Bidentate bicarbonate and
- Monodentate bicarbonate.

During the concentration swing adsorption/desorption process at 25°C of the above process the bidentate bicarbonate and monodentate bicarbonate were observed to be the major surface species formed and decomposed. The temperature-programmed-desorption revealed that the monodentate and bidentate bicarbonate are bounded stronger to the diamine grafted SBA-15 surface than the bidentate carbonate.

Khatri et al. transmission IR spectra reveals the isolated hydroxyl groups (Silanol groups) with wavenumber $3750cm^{-1}$ in Figure 3-1, which reacts with a variety of functional groups. This is usually tailored towards the surface chemistry of silica and glass material.

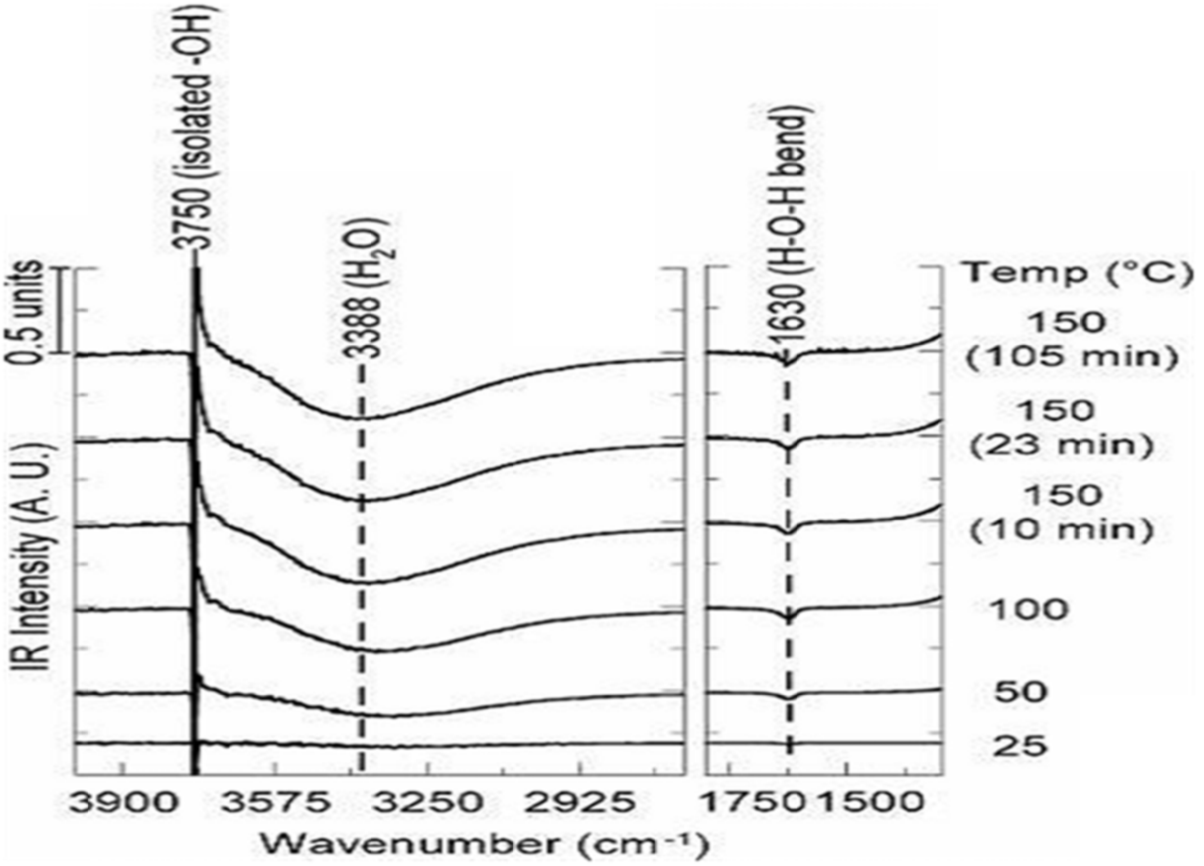


Figure 3-1: Transmission IR spectra of SBA-15 during Heating from 25°C to 150°C [63]

Figure 3-2 reveals the decrease in the isolated surface hydroxyl group at wavenumber $3745 cm^{-1}$, suggesting the reaction of the surface hydroxyl groups (Si-OH) with highly active methoxy groups of the secondary amine (diamine) compound. The reaction for the above reaction is presented below [44, 63]:

$$(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2 + 3SiOH \rightarrow$$

$$(SiO)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2 + 3CH_3OH \quad (1)$$

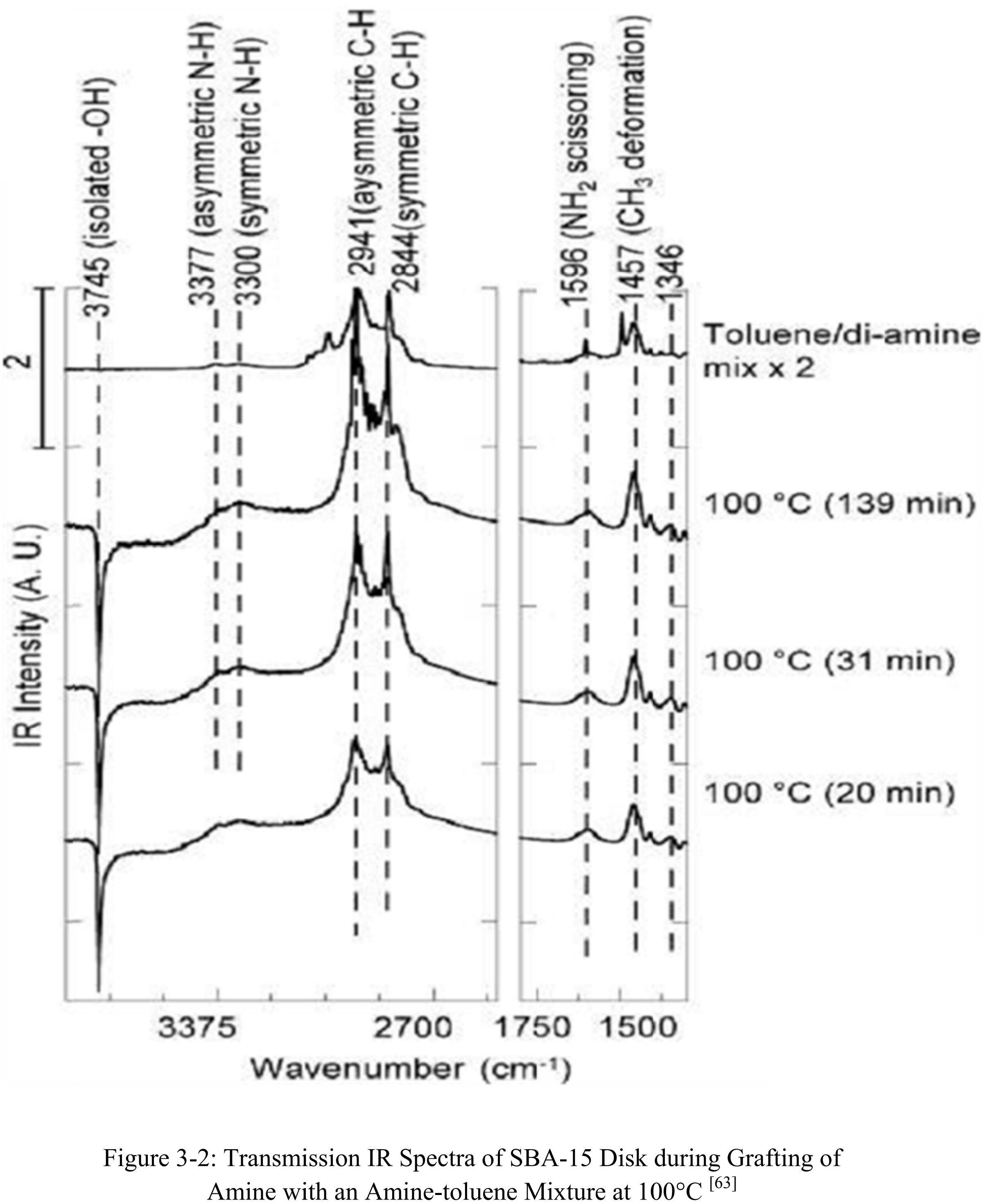


Figure 3-2: Transmission IR Spectra of SBA-15 Disk during Grafting of Amine with an Amine-toluene Mixture at 100°C [63]

This was further verified by the small amount of methanol formed, which is evident by the OH bending vibration of methanol at wavenumber $1346 cm^{-1}$.

Khatri et al. [63] concluded that the isolated surface hydroxyl functional group were the active moieties on the SBA-15 surface for the reaction with the methoxy groups on the "diamine-containing silanes" and that the capture of CO_2 on the grafted diamine surface was twice that of the mono-amine grafted SBA-15 in the TSA process of $25^{\circ}C$ to $120^{\circ}C$ temperature range.

Gray et al. [30] studied CO_2 capture from simulated gas stream on immobilized and aminated SBA-15 solid sorbent. The results obtained suggested that immobilized secondary amines had stronger affinity for CO_2 capture from flue gas stream than primary amines, though the performance of the sorbent decreased with regeneration.

In comparing the various sorbents, Tables 3-1, 3-2 and 3-3 present the following:

- A summary of amine-grafted silica-based adsorbent prepared under anhydrous conditions and applied for CO_2 adsorption [62].
- A summary of water-aided amine-grafted silica adsorbents applied to CO_2 adsorption [62] and
- A summary of amine-grafted silica based adsorbents for CO_2 adsorption performance [62].

One important concept involved in the grafting process was considered by Harlick et al [62]. Herein, they compare the use of water during the grafting process and anhydrous grafting. In terms of concept, dry grafting procedure could be considered as a reaction between the surface hydroxyl groups and the alkoxy ligands of the silane compound, thus leading to the formation of a tethered surface layer of amine functionalities. Invariably, it is assumed that the entire alkoxy ligands would ideally react with the hydroxyl groups on the surface to release the corresponding alcohol, thereby leading to the formation of $(SiO)_3Si\text{-}R$ species, See Figure 3-3. (Note: this is under the assumption of the formation of $(SiO)_3Si\text{-}R$ surface species, where the support chemistry $(SiO)_x$ was systematically represented by the pore wall for simplicity).

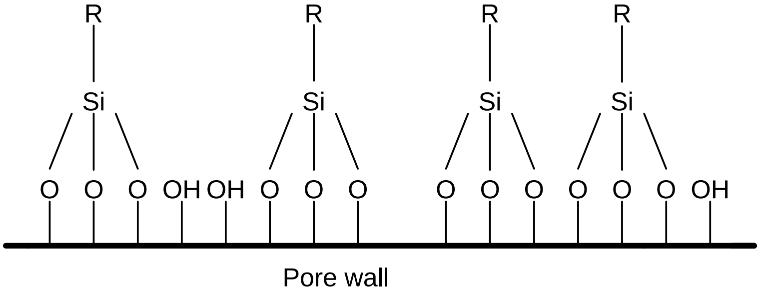


Figure 3-3: Ideal Pore Surface Obtained from Anhydrous Alkoxy-silane Grafting [62]

Normally, the reaction should occur with a 3:1 ratio of surface OH to silane grafted on the compound. However, this is not often achieved, reason being that one or two alkoxy groups per silane may not react; see Figure 3-4. (Where the support chemistry $(SiO)_x$ was represented as pore wall for simplicity).

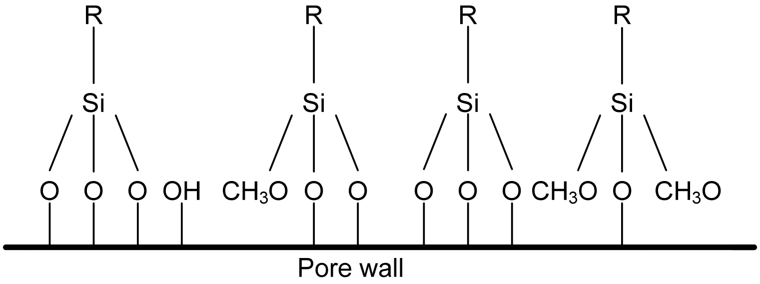


Figure 3-4: Structure of Proposed Surface Obtained with Anhydrous Grafting [62]

For a complete consumption of the free alkoxy ligands and total surface coverage, water may be added to the support material in order to produce a hydrated surface [62]. This increases the surface density of the hydroxyl groups or initiates the hydrolysis of unreacted alkoxy groups with the free silane present in the solvent phase. Invariably, this enhances the surface coverage of the amine bearing species, unlike the perfect monolayer concept proposed by Feng et al. [69]. See Figure 3-5.

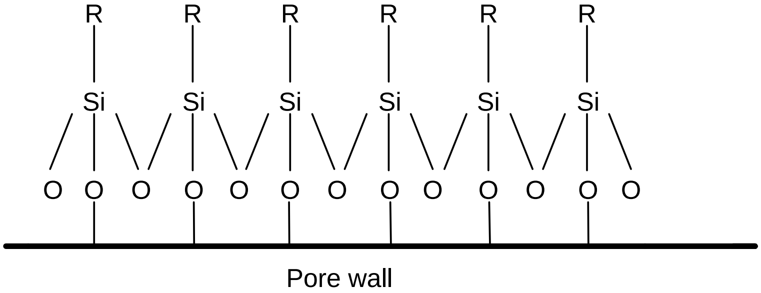


Figure 3-5: Proposed Idealized Fully Cross-linked Pore Surface Obtained for Alkoxy-silane Grafted in the Presence of Water [69]

Harlick et al. [62] was of the opinion that grafting in the above process i.e. under these conditions is more complex. Thus, the grafting should be considered as a coating since there is a possibility that the aminosilanes are not directly attached to the surface, rather only through the Si-O-Si bridges to the other grafted aminosilane; see Figure 3-6. (Note: The akyl (R) group denotes the triamine chain, with the dash lines representing the out of plane orientation of the bold groups; thus approximating the depth).

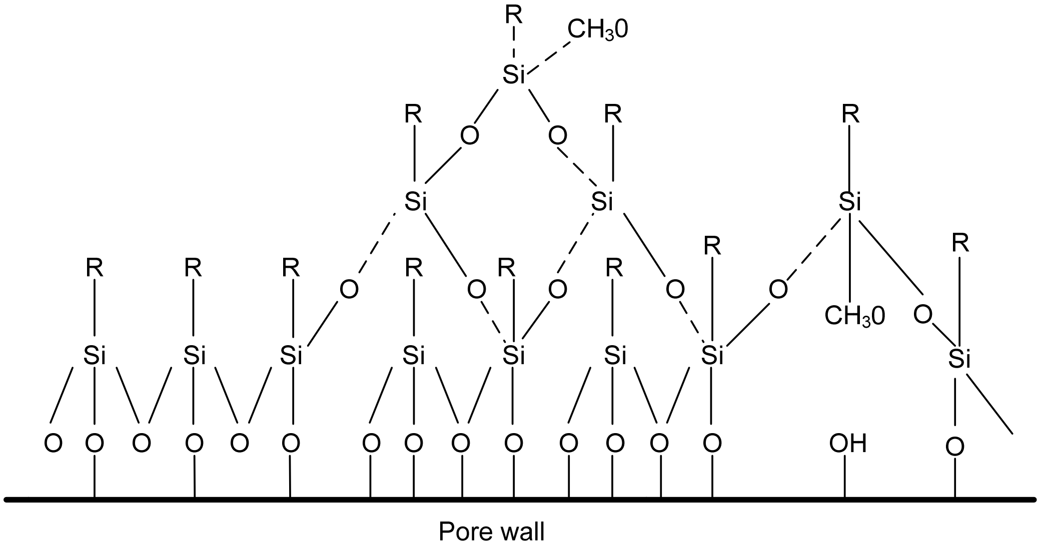


Figure 3-6: Proposed Early Stage Growth of a 3-D Polyaminosilane Layer Occurring during Grafting of Alkoxy-silane Compounds in the Presence of Water [62]

3.3 Amine grafted sorbent CO_2 interaction

With reference to the gas-liquid absorption process, the proposed reaction sequences [64] for the reaction of primary or secondary alkanolamines with CO_2 are shown in Figure 3-7 below.

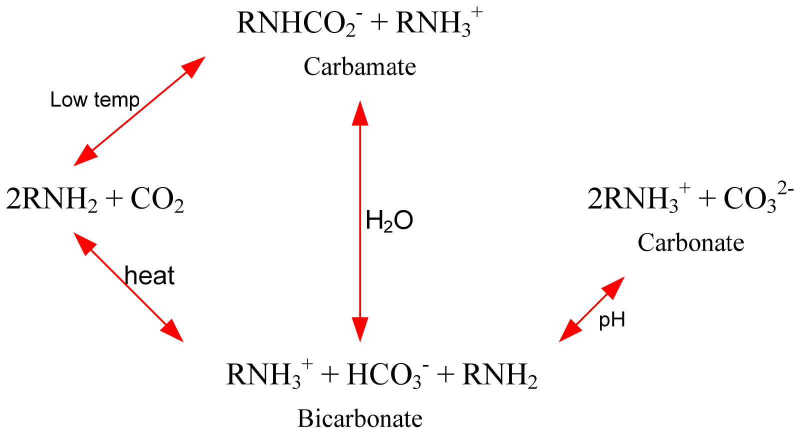


Figure 3-7: Proposed Reaction Sequence for CO_2 Capture by Liquid Amine-based System [30]

From Figure 3-7, majority of the CO_2 captured results in the formation of bicarbonate in the liquid amine capture systems. In aqueous media, 2 moles of amine/mole of CO_2 is required for the formation of stable bicarbonate compounds resulting in the capture of CO_2 [64].

Generally, primary aqueous alkanolamines can react stochiometrically with CO_2 by the following reaction [63]:

$$C_2H_4OHNH_2 + CO_2 + H_2O \longleftrightarrow C_2H_4OHNH_3^+ + HCO_3^- \qquad (2)$$

Gray et al. stated that "solid-amine CO_2 sorbents should have similar reaction with gaseous CO_2, water vapor and the amine site on its surface".

From the IR analysis on the mechanism of diamine grafting on SBA-15 by Khatri et al, it was reported that the isolated surface hydroxyl groups where the active moieties on the surface of the SBA-15 for the reaction with methoxy groups of the diamine-containing silanes. (See Figures 3-1 and 3-2). The adsorbed CO_2 on the primary and secondary amine groups resulted in the formation of carbonate, bicarbonate and carbamic acids (See Figure 3-7 above). The IR spectra by Chang et al, (Figure 3-8) shows the adsorption of CO_2 on a fresh APTS-SBA-15. Wavenumber 1634cm^{-1} represents the bidentate bicarbonate product formed via the surface reaction of CO_2 with the sorbent[44]. The bidentate carbonate has peak at wavenumbers 1575 and 1390cm^{-1} and monodentate carbonate at 1337cm^{-1} [44].

Bands in 1595, 1440, and 1330cm^{-1} regions may be associated with carbamic acid [44]. The bond energy reported for the carbamic acid C-N bond was at the level of 300kJ/mol [44] which is higher than the heat of adsorption of CO_2 on the surface of the sorbent.

The carbamic acid (RNHCOOH) was suggested as the precursor for the formation of R-NH_3^+ species involving the following steps [44]:

$$RNH_2 + CO_2 \rightarrow RNHCOOH \tag{3}$$

R in Equation (3) above symbolizes the alkyl group.

$$RNHCOOH + RNH_2 \rightarrow RNCOO^- + RNH_3^+ \tag{4}$$

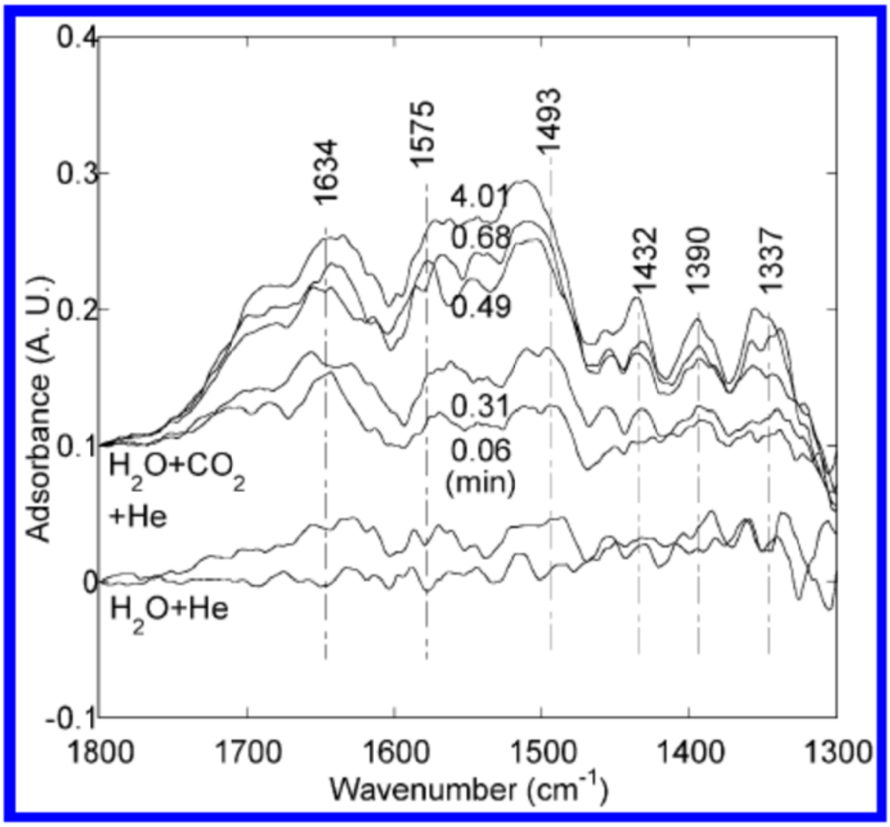


Figure 3-8: Infrared Spectra of CO_2 Adsorbed on Fresh APTS-SBA-15 Sorbent [44]

The CO_2 also reacts with H_2O and OH^- to form HCO_3^- and CO_3^{2-} [93].

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \tag{5}$$

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{6}$$

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \tag{7}$$

Chang et al, suggested that the interaction between HCO_3^- and CO_3^{2-} with $(Si\text{-}O)_3\text{-}SiCH_2CH_2CH_2NH_3^+$ could result in the formation of adsorbed carbonate and bicarbonate. See Table 3-4 below.

According to Khatri et al, the major species formed by the surface adsorption of CO_2 on the diamine grafted SBA-15 sorbent are the monodentate bicarbonate, bidentate bicarbonate and bidentate carbonate. A stronger bond exists between the bidentate bicarbonate species and the diamine grafted SBA-15 than bidentate carbonate.

Table 3-1: Summary of Amine-Grafted Silica-Based Adsorbents Prepared Under Anhydrous Conditions and Applied

		Initial support properties			Grafting condition			Amount grafted (amine content^e)			
Support Material	Amine type^b	BET SA^c (m^2/g)	Pore diameter (nm)	Pore volume^c (cm^3/g)	Silanex added^c (cm^3/g)	n^c (vol%[silane]/g)	Temp (^oC)	Organic^d (mmol/g)	mmol(N)/g	μmol(N)/m^2	Reference
Silica gel	mono-ethoxy	340	12.0	1.4	0.45	0.0	138	1.20	1.20	3.53	46
Xerogel	mono-ethoxy	816	n/a		5.0	10.0	70	1.70	1.70	2.08	31
HMS^g	mono-ethoxy	762	3.0	1.02	4.0	4.0	25.0	1.93	1.93	2.53	65
HMS^g	mono-ethoxy	1198	2.0	0.97	4.0	4.0	25.0	2.29	2.29	1.91	65
MCM-48^h	mono-ethoxy	1389	n/a		5.0	10.0	70	2.30	2.30	1.66	31
MCM-48^h	mono-ethoxy	1290	2.6	1.15		0.0	110.0	2.45	2.45	1.90	52
SBA-15^i	mono-ethoxy	910	5.9	1.11	8.5	3.4	110.0	2.57	2.57	2.82	70
MCM-48^{f,h}	tert	1290	2.6	1.15		0.0	110.0	1.48	1.48	1.15	52
HMS^g	di	762	3.0	1.02	3.9	3.9	25.0	1.54	3.07	4.03	71
HMS^g	di	1268	2.4	0.98	3.0	3.0	25.0	1.82	3.64	2.87	71
SBA-15^i	di	910	5.9	1.11	8.5	3.4	110.0	1.88	3.76	4.13	70
MCM-48^{f,h}	PEI	1290	2.6	1.15		0.0	110.0		5.20	4.03	52
SBA-15^i	tri	910	5.9	1.11	8.5	3.4	110.0	1.62	4.85	5.33	70
HMS^g	tri	762	3.0	1.02	4.9	4.9	25.0	1.29	3.86	5.06	72
HMS^g	tri	1268	2.4	0.98	3.0	3.0	25.0	1.52	4.57	3.61	72
MCM-41^h	tri	1140	3.7	1.03	3.0	2.0	70.0	1.92	5.75	5.04	62
MCM-41^h	tri	1140	3.7	1.03	3.0	2.0	85.0	1.98	5.95	5.22	62
MCM-41^h	tri	1140	3.7	1.03	3.0	2.0	95.0	1.94	5.83	5.11	62
MCM-41^h	tri	1140	3.7	1.03	3.0	2.0	110.0	1.90	5.69	4.99	73
PE-MCM-41^{h,j}	tri	950	10.0	2.21	3.0	2.0	70.0	2.02	6.07	6.39	62
PE-MCM-41^{h,j}	tri	950	10.0	2.21	3.0	2.0	85.0	2.04	6.11	6.43	62
PE-MCM-41^{h,j}	tri	950	10.0	2.21	3.0	2.0	95.0	2.01	6.03	6.35	62
PE-MCM-41^{h,j}	tri	950	10.0	2.21	3.0	2.0	110.0	1.99	5.98	6.29	73

[a] Reflects the most studied material and a group of materials presented by the authors. In some instances, a second entry is shown for the highest performing material.

[b] Mono = either aminopropyltriethoxysilane or aminopropyltrimethoxysilane;
di = aminoethylaminopropyltrimethoxysilane;
tri = aminoethylaminoethylaminopropyltrimethoxysilane;
tert = tertiary functionality,
PEI = polyethyleneimine.

[c] Units are per gram of SiO_2 (support).

[d] Units are mmol of organic chain per gram of final material (i.e. organic + SiO_2), with the alkoxy groups absent.

[e] Units are in mmol of amine (nitrogen) per gram of final material (i.e. aminosilane + SiO_2) or per square meter of the surface area of the initial support.

[f] Chloropropyltrimethoxysilane was first grafted at 110^{o}C, then PEI or pyrrolidine reacted with the chloride group to produce the desired tethered amine functionality.

[g] HMS: hexagonal mesoporous silica support.

[h] MCM: Mobil Crystalline Materials.

[i] SBA-15: a mesoporous silicate.

[j] PE- MCM-41: pore-expanded MCM-41.

Table 3-2: Summary of Amine-Grafted Silica-Based Adsorbents Applied to CO_2 Adsorption[a]

		Initial support properties			Grafting condition				Amount grafted (amine content[d])		
Support Material	Amine type[b]	BET SA[c] (m^2/g)	Pore diameter (nm)	Pore volume[c] (cm^3/g)	Silane added[c] (cm^3/g)	Water[c] (cm^3/g)	H_2O/alkoxy[c] (mol/mol)	Temp (°C)	mmol(N)/g	μmol(N)/m^2	Reference
MCM-48[e]	mono-ethoxy	1290	2.6	1.15			1.00	110.0	3.99	3.09	52
SBA-15[f]	mono-ethoxy	820	5.9	1.07	8.5	preboiled		110.0	2.61	3.18	70
SBA-15[f]	di	700	6.7		1.0	0.32	1.28	110.0	2.64	3.77	74
SBA-15[f]	di	820	5.9	1.07	8.5	preboiled		110.0	4.61	5.62	70
SBA-15[f]	tri	820	5.9	1.07	8.5	preboiled		110.0	5.80	7.07	70
PE-MCM-41[g]	tri	950	10.0	2.21	3.0	0.30	0.48	70.0	7.75	8.16	62
PE-MCM-41[g]	tri	950	10.0	2.21	3.0	0.30	0.48	85.0	7.98	8.40	62
PE-MCM-41[g]	tri	950	10.0	2.21	3.0	0.20	0.32	95.0	6.75	7.11	62
PE-MCM-41[g]	tri	950	10.0	2.21	3.0	0.20	0.32	110.0	6.65	7.00	62

[a] Reflects the most studied material and a group of materials presented by the authors. In some instances, a second entry is shown for the highest performing material.

[b] Mono = either aminopropyltriethoxysilane or aminopropyltrimethoxysilane;
di = aminoethylaminopropyltrimethoxysilane;
tri = aminoethylaminoethylaminopropyltrimethoxysilane;.

[c] Units are per gram of SiO_2 (support).

[d] Units are mmol of amine (nitrogen) per gram of final material (aminosilane + SiO_2) or per square meter of the surface area of the initial support.

[e] MCM: Mobil Crystalline Materials.

[f] SBA-15: a mesoporous silicate.

[g] PE- MCM-41: pore-expanded MCM-41.

Table 3-3: Summary of Amine-Grafted Silica-Based Adsorbents CO_2 Adsorption Performance ^{a,b}

			CO_2 adsorption performance						Humid CO_2		CO_2/N ratio		
	Support Material	Amine type^{c}	CO_2 partial Pressure^{d} (kPa)	Balance gas	Temp (^{o}C)	Dry capacity (mmol/g)	Max rate (mmol/g/min)	Adsorption parameter (mmol/g/Pa)	R.H.(%)	Adsorption capacity (mmol/g)	Dry ads (mol/mol)	Wet ads (mol/mol)	Reference
Anhydrous grafting	Silica gel	mono	101		295	0.41		4.02	98	0.89	0.338	0.744	46
	Xerogel	mono	101		298	1.12		11.00			0.656	0.000	31
	HMS^{g}	mono	91	Ar	293	0.86		9.47	30.0	1.04	0.448	0.537	65
	HMS^{g}	mono	91	Ar	293	1.59		17.50			0.696		65
	MCM-48^{h}	mono	5	He	298	1.14		223.00	64	2.30	0.494	1.000	31
	MCM-48^{h}	mono	101		298	0.80		7.92			0.327		52
	SBA-15^{i}	mono	15	N_2	333	0.52		34.70	61.0	0.50	0.202	0.195	70
	MCM-48^{c,h}	tert	101		298	0.30		2.97			0.145		52
	HMS^{g}	di	91	Ar	293	0.89		9.74	30.0	0.45	0.289	0.148	71
	HMS^{g}	di	91	Ar	293	1.66		18.20			0.455		71
	SBA-15^{i}	di	15	N_2	333	0.87		58.00	61.0	0.90	0.231	0.239	70
	MCM-48^{c,h}	PEI	101		298	0.40		3.96			0.077		52
	SBA-15^{i}	tri	15	N_2	333	1.10		73.30	61.0	1.21	0.227	0.249	70
	HMS^{g}	tri	91	Ar	293	1.20		13.20	30.0	0.98	0.312	0.253	72
	HMS^{g}	tri	91	Ar	293	1.34		14.70			0.293		72
	MCM-41^{h}	tri	5	N_2	298	1.04	0.841	203.00	27.0	1.12	0.180	0.195	62
	MCM-41^{h}	tri	5	N_2	298	1.08	0.865	211.00	27.0	1.18	0.181	0.198	62
	MCM-41^{h}	tri	5	N_2	298	1.01	0.823	198.00	27.0	1.09	0.173	0.186	62
	MCM-41^{h}	tri	5	N_2	298	0.97	0.802	190.00	27.0	1.01	0.170	0.185	73
	PE-MCM-41^{h,j}	tri	5	N_2	298	1.51	0.947	296.00	27.0	1.60	0.249	0.264	62
	PE-MCM-41^{h,j}	tri	5	N_2	298	1.55	0.963	304.00	27.0	1.66	0.254	0.272	62
	PE-MCM-41^{h,j}	tri	5	N_2	298	1.47	0.952	288.00	27.0	1.58	0.244	0.263	62
	PE-MCM-41^{h,j}	tri	5	N_2	298	1.41	0.951	276.00	27.0	1.52	0.236	0.254	73

Water aided grafting	MCM-48[h]	tri	5	N_2	298	0.10		0.99			0.025		52
	SBA-15[i]	mono	101	N_2	333	0.66		44.00	61.0	0.65	0.253	0.249	70
	SBA-15[i]	mono	15	N_2	298	0.57		37.90	64.0	0.57	0.215	0.215	74
	SBA-15[i]	di	15	N_2	333	1.36		90.70	61.0	1.51	0.295	0.328	70
	SBA-15[i]	di	15	N_2	333	1.58		105.00	61.0	1.80	0.272	0.310	70
	PE-MCM-41[h, j]	tri	15	N_2	298	2.33	1.553	457.00	27.0	2.58	0.301	0.333	62
	PE-MCM-41[h, j]	tri	5	N_2	298	2.65	1.79	520.00	27.0	2.94	0.332	0.368	62
	PE-MCM-41[h, j]	tri	5	N_2	298	1.89	1.256	371.00	27.0	2.08	0.280	0.309	62
	PE-MCM-41[h, j]	tri	5	N_2	298	1.69	1.1	331.00	27.0	1.85	0.254	0.278	62
Zeolite	13X[f]		5	N_2	298	2.05	0.84	402.00	27.0	0.09			75
	13X[f]		101		298	4.70		46.50	27.0	0.09			75

[a] Reflects the most studied material and a group of materials presented by the authors. In some instances, a second entry is shown for the highest performing material.

[b] Denotes that the order of the material is identical in Table 3-2 and 3-3 for each grafting type.

[c] Mono = either aminopropyltriethoxysilane or aminopropyltrimethoxysilane;
di = aminoethylaminopropyltrimethoxysilane;
tri = aminoethylaminoethylaminopropyltrimethoxysilane;
tert = tertiary functionality,
PEI = polyethyleneimine.

[d] Total system polyethyleneimine.

[e] Chloropropyltrimethoxysilane was first grafted at 110°C, then PEI or pyrrolidine reacted with the chloride group to produce the desired tethered amine functionality.

[f] Regenerated at 200°C for 1 hour in Nitrogen gas stream.

[g] HMS: hexagonal mesoporous silica support.

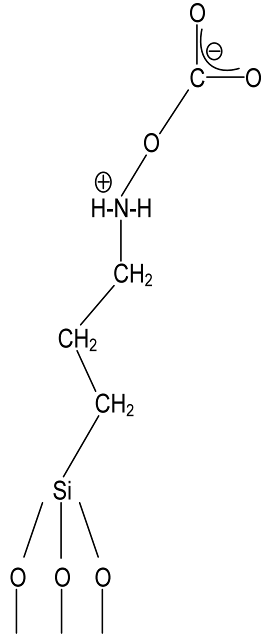
[h] MCM: Mobil Crystalline Materials.

[i] SBA-15: a mesoporous silicate.

[j] PE- MCM-41: pore-expanded MCM-41.

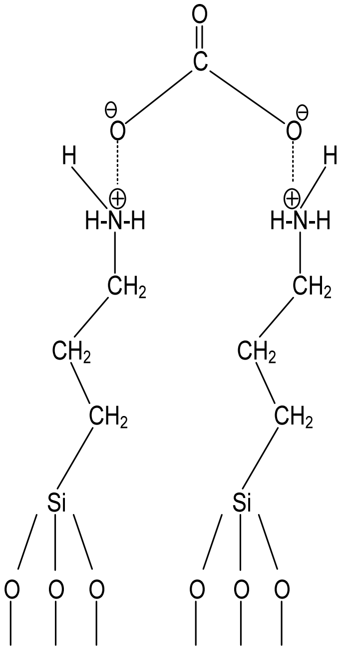
Table 3-4: Proposed Adsorbed Species on the APTS-SBA-15 Surface [44]

Monodentate Carbonate



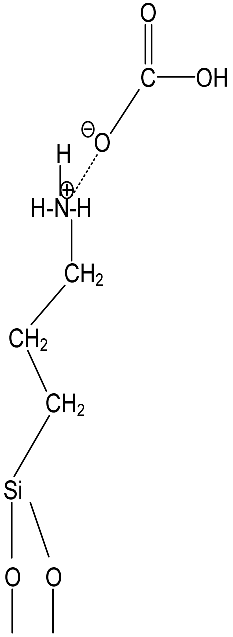
1337cm^{-1}

Bidentate Carbonate



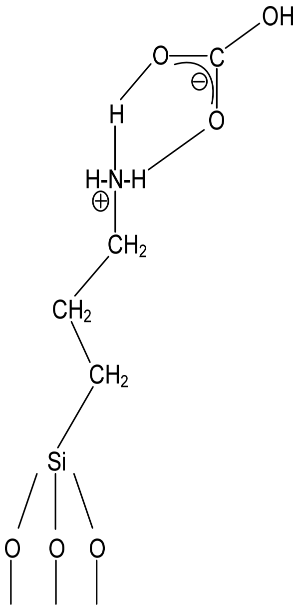
1575, 1390cm^{-1}

Monodentate Bicarbonate



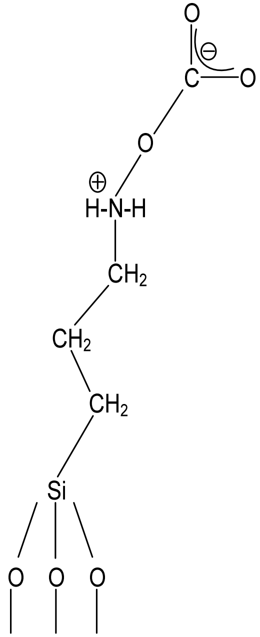
1493, 1432cm^{-1}

Bidentate Bicarbonate



1634cm^{-1}

Carbamic acid



1595, 1441, 1330cm^{-1}

4 CONCLUSION AND RECOMMENDATION

Based on the review of the various literatures, the following can be concluded:

1. Compared to amine-based liquid solvents, solid sorbents have higher mass transfer rate and adsorption capacity, thus resulting in smaller bed thereby significantly minimizing construction and equipment cost. They also require less energy for regeneration thereby eliminating the problems related to corrosion and equipment degradation, thus making sorbent more cost-effective.
2. For efficient and economical CO_2 capture technology, sorbent should have a CO_2 adsorption capacity of within the range of 1000-2000μmol/g or above, together with a long-term regeneration capacity, and a small difference in adsorption and desorption temperatures in a flue gas environment. For economic viability, the cost of sequestration should be \$10 a ton of CO_2 from stationary sources for solid sorbents. The CO_2 capture unit of a power plant should be located after the flue-gas desulfurization unit. Based on some assumptions, a rough estimate was made with regards to the size of both the adsorption and regeneration units for a 500MW coal fired power plant. Check the appendix for their estimated size.
3. The larger surface area of the sorbent support, the greater amount of active sites available for grafting, thus implying a sorbent support with larger surface area would result in more active sites for amine functionality and a higher CO_2 adsorption capacity.
4. Higher CO_2 adsorption capacity has been reported for solid sorbent support grafted with secondary amines compared to grafting with primary amine.
5. Compared with activated carbon, amine-grafted sorbents have a higher CO_2 selectivity.

6. The presence of water vapor in the gas stream during grafting and/or during CO_2 adsorption can improve the CO_2 adsorption capacity of the amine-grafted sorbents, which is an advantage of amine-grafted sorbents over conventional zeolite.
7. The most promising result under anhydrous grafting condition was that of MCM-48 silica grafted with 3-aminopropyltriethoxysilane by Huang et al [31], having a CO_2 adsorption capacity of 2.30mmol/g sorbent on a basis of total adsorbent weight.
8. The most promising result under wet grafting condition was that of TRI-PE-MCM-41 by Harlick et al [62], having a CO_2 adsorption capacity of 2.94mmol/g.

Based on literature review, it is reported that amine-grafting process can boost CO_2 adsorption on a silane sorbent support [30, 31, 44, 62, 63]. Also the presence of a significant amount of organic and silica compounds on the heterogeneous surface of biochar has been reported [11], which could potentially make biochar a promising sorbent support for amine grafting. Biochar can be obtained from plant materials and waste feedstock, such as sorghum, switchgrass, miscanthus, bamboo, corn stover etc., which are relatively available. Hence, it is highly recommended that the impregnation of amine on the surface of biochar for CO_2 adsorption be considered for future research purpose.

LIST OF REFERENCES

1. IPCC, 1996, Climate Change 1995: The Science of Climate Change. J.T Houghton et al., eds. Cambridge University Press, Cambridge.
2. DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update. September 2010.
3. Zhang Z., Huang S., Xian S., Xi H., and Li Z.. Adsorption Equilibrium and Kinetics of CO_2 on Chromium Terephthalate MIL-101. Energy & Fuels, 2011, 25 (2), 835–842.
4. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press. 2005.
5. Xu X. and Moulijn J.A.. Mitigation of CO_2 by Chemical Conversion: Plausible Chemical Reactions and Promising Products. Energy & Fuels, 1996, 10, pp305-325.
6. Yang R.T.. Gas Separation by Adsorption Processes. Imperial College Press. 1987, pp9, 238-240.
7. Plaza M.G., Pevida C., Arenillas A, Rubiera F., Pis J.J.. CO_2 Capture by Adsorption with Nitrogen Enriched Carbons. Fuel, 2007, 86, 2204-2212.
8. Zhang Z., Xu M., Wang H., Li, Z.. Enhancement of CO_2 Adsorption on High Surface Area Activated Carbon Modified by N_2, H_2 and Ammonia. Chemical Engineering Journal, 2010, 160, 571-577.
9. Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., Yaghi, O. M.. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. Science, 2002, 295, 469–472.
10. Karra, J. R., Walton, K. S.. Effect of Open Metal Sites on Adsorption of Polar and Nonpolar Molecules in Metal−Organic Framework Cu-BTC. Langmuir, 2008, 24(16), 8620–8626.

11. Hammes K., Schmidt M.. Changes of Biochar in Soil. In: Lehmann J., Joseph S. (eds.). Biochar for Environmental Management: Science and Technology. Earthscan. 2009, 169-178.
12. Wang L.; Yang R.. New Sorbents for Hydrogen Storage by Hydrogen Spillover – A Review. Energy & Environmental Science, 2008, 54, 268–279.
13. Kusgens P., Rose M., Senkovska I., Frode H., Henschel A., Siegle S., Kaskel S.. Characterization of Metal-organic Frameworks by Water Adsorption. Microporous & Mesoporous Materials, 2009, 120(3), 325–330.
14. Sohi S., Lopez-Capel E., Krull E., Bol R.. Biochar, Climate Change and Soil: A Review to Guide Future Research. CSIRO Land and Water Science Report 05/09. February 2009.
15. Bagreev A., Bandosz T.J., Locke D.C.. Pore Structure and Surface Chemistry of Adsorbents Obtained by Pyrolysis of Sewage Sludge Derived Fertilizer. Carbon, 2001, 39(13), 1971-1977.
16. Hitoshi T., Ai F., Haruo H.. Development of Advanced Utilization Technologies for Organic Waste: (Part 1) Greenhouse Gas and Nutrient Salt Adsorption Properties of Wood-based Charcoal. Denryoku Chuo Kenkyujo Abiko Kenkyujo Hokoku, Research Report of Abiko Research Laboratory, 2002(U02010), 17.
17. Skarstrom C.W.. Method and Apparatus for Fractionating Gaseous Mixtures by Adsorption. U.S. Patent 2944627, to Esso Research and Engineering Company. 1960.
18. Maontgareuil P., Domine D.. Process for Separating a Binary Gaseous Mixture by Adsorption. U.S. Patent 3155468, to L'Air Liquide, Societe Anonyme por l'etude et l'Exploitation des Procedes Georges Claude, Paris. 1964.

19. Walton-on-Thames M., Guildford A., Allentown T.. Temperature Swing Adsorption. U.S. Patent 5846295, to Air Products and Chemicals, Inc., Allentown, Pa. 1998.
20. Paris M.G., Notre Dame de Gravenchon S.G., Chatenay Malabry P.P., Paris F.V.. Process and Apparatus for Purifying Air to Be Distilled by Adsorption. U.S. Patent 5137548, to L'Air Liquide, Societe Anonyme por l'etude et l'Exploitation des Procedes Georges Claude, Paris. 1992.
21. Grande C. A., Rodrigues A. E. Electric Swing Adsorption for CO_2 Removal from Flue Gases. International Journal of Greenhouse Gas Control, 2007, 2(2), 194-202.
22. Ishibashi M., Ota H., Akutsu N., Umeda S., Tajika M.. Technology for Removing Carbon Dioxide from Power Plant Flue Gas by Physical Adsorption Method. Energy Conversation & Management, 1996, 37(6-8), 929-933.
23. Petrovska M., Tondeur D., Grevillot G., Granger J., Mitrovic M.. Temperature Swing Gas Separation with Electrothermal Desorption Step. Separation Science & Technology, 1991, 26(3), 425-444.
24. Sullivan, P.D.. Organic Vapor Recovery Using Activated Carbon Fiber Cloth and Electrothermal Desorption. Ph.D. Dissertation, University of Illinois at Urbana. 2003.
25. Merel J., Clausse M., Meunier F.. Carbon Dioxide Capture by Indirect Thermal Swing Adsorption Using 13X Zeolite. Environmental Progress, 2006, 25(4), 327-333.
26. Ettlili N., Bertelle S.. A New Electric Swing Adsorption Process for Post Combustion CO_2 Capture. In: Proceedings of the 8th International Conference on Greenhouse Gas Control Technologies, Elsevier, ISBN: 0-08-046407-6. 2006.
27. Bonnissel M.P., Luo L., Tondeur D.. Rapid Thermal Swing Adsorption. Industrial & Engineering Chemistry Research, 2001, 40(10), 2322-2334.

28. Saysset S., Grevillot G., Lamine A.S.. Adsorption of Volatile Organic Compounds on Carbonaceous Adsorbent and Desorption by Direct Joule Effect. Recent Progress in Genie des Procedes, No. 68 Proceedings of the 2nd European Congress of Chemical Engineering, Montpellier, France, 1999, 389–396.
29. Yu F. D., Luo L., Grevillot G.. Electrothermal Swing Adsorption of Toluene on an Activated Carbon Monolith. Experiments and Parametric Theoretical Study. Chemical Engineering & Processing, 2007, 46, 70–81.
30. Gray M.L., Soong Y., Champagne K.J., Pennline H., Baltrus J.P., Stevens R.W.Jr., Khatri R., Chuang S.S.C., Filburn T.. Improved Immobilized Carbon Dioxide Capture Sorbents. Fuel Processing Technology, 2005, 86, 1449–1455.
31. Huang H. Y., Yang R. T., Chinn D., Munson C. L.. Amine-Grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas. Industrial & Engineering Chemistry Research, 2003, 42, 2427-2433.
32. Maddox R. N., Mains G. J., Rahman M. A.. Reactions of Carbon Dioxide and Hydrogen Sulfide with Some Alkanolamines. Industrial & Engineering Chemistry Research, 1987, 26(1), 27–31.
33. Haimour N., Sandall O. C.. Absorption of H2S into Aqueous Methyldiethanolamine. Chemical Engineering Communications, 1987, 59, 85-93.
34. Pani F., Gaunand A., Richon D., Cadours R., Bouallou C.. Absorption of H_2S by an Aqueous Methyldiethanolamine Solution at 296 and 343 K. Journal of Chemical and Engineering Data, 1997, 42, 865-870.
35. Posey M. L., Tapperson K. G., Rochelle G. T.. Simple Model for the Prediction of Acid Gas Solubilities in Alkanolamines. Gas Separation & Purification, 1996, 10(3), 181-186.

36. Bhide B. D., Voskericyan A., Stern S. A.. Hybrid Processes for the Removal of Acid Gases from Natural Gas. Journal of membrane science, 1998, 140(1), 27-49.
37. Tontiwachwuthikul P., Meisen A., Lim C. J.. Solubility of Carbon Dioxide in 2-Amino-2-methyl-1-propanol Solutions. Journal of Chemical and Engineering Data, 1991, 36, 130-133.
38. Blauwhoff P. M. M., Versteeg G. F., Van Swaaij W. P. M.. A Study on the Reaction between CO_2 and Alkanolamines in Aqueous Solutions. Chemical Engineering Science, 1984, 39(2), 207–225.
39. Veawab A., Tontiwachwuthikul P, Chakma A.. Corrosion Behavior of Carbon Steel in the CO_2 Absorption Process Using Aqueous Amine Solutions. Industrial & Engineering Chemistry Research, 1999, 38, 3917-3924.
40. Satyapal S., Filburn T., Trela J., Strange J.. Performance and Properties of a Solid Amine Sorbent for Carbon Dioxide Removal in Space Life Support Applications. Energy & Fuels, 2001, 15, 250-255.
41. Birbara P. J., Filburn T. P., Nalette T. A.. Regenerable Solid Amine Sorbent. U.S. Patent 5876488, to United Technologies Corporation, Hartford, conn. 1999.
42. Birbara P. J., Nalette T. A.. Regenerable Supported Amine-polyol Sorbent. U.S. Patent 5492683, to United Technologies Corporation, Windsor Locks, conn. 1996.
43. Soong Y., Gray M. L., Siriwardane R. V., Champagne K. J., Stevens R. W. Jr., Toochinda P., Chuang S. S. C.. A Novel Solid Sorbents for CO_2 Capture. Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry, 2001, 46, 285-286.

44. Chang A. C., Chuang S. C., Gray M., Soong Y.. In-Situ Infrared Study of CO_2 Adsorption on SBA-15 Grafted with γ-(Aminopropyl)triethoxysilane. Energy & Fuels, 2003, 17, 468-473.
45. Niswander R. H., Edwards D. J., DuPart M. S., Tse J. P.. A More Energy Efficient Product for Carbon Dioxide Separation. Separation Science and Technology, 1993, 28, 565-578.
46. Leal O., Bolivar C., Ovalles C., Garcia J. J., Espidel Y.. Reversible Adsorption of Carbon Dioxide on Amine Surface-bonded Silica Gel. Inorganica Chimica Acta, 1995, 240, 183-189.
47. Tepper F., Udavcak R. J., Vancheri F. J., Ball K. E.. Regenerable Carbon Dioxide Sorbents. Aerospace Medicine, 1969, 40, 297-300.
48. Kikkinides E. S., Yang R. T., Cho S. H.. Concentration and Recovery of Carbon Dioxide from Flue Gas by Pressure Swing Adsorption. Industrial & Engineering Chemistry Research, 1993, 32, 2714-2720.
49. Kikkinides E. S., Sikavitsas V. I., Yang R. T.. Natural Gas Desulfurization by Adsorption: Feasibility and Multiplicity of Cyclic Steady States. Industrial & Engineering Chemistry Research, 1995, 34, 255-262.
50. Chen, Y. D.; Ritter, J. A.; Yang, R. T. Nonideal Adsorption from Multicomponent Gas Mixtures at Elevated Pressures on a 5A Molecular Sieve. Chemical Engineering Science, 1990, 45, 2877-2894.
51. Chue K. T., Kim J. N., Yoo Y. J., Cho S. H., Yang R. T.. Comparison of Activated Carbon and Zeolite 13X for CO_2 Recovery from Flue Gas by Pressure Swing Adsorption. Industrial & Engineering Chemistry Research, 1995, 34, 591-598.

52. Jaroniec C. P., Kruk M., Jaroniec M., Sayari A.. Tailoring Surface and Structural Properties of MCM-41 Silicas by Bonding Organosilanes. Journal of Physical Chemistry B, 1998, 102, 5503-5510.
53. Cauvel A., Renard G., Brunel D.. Monoglyceride Synthesis of Heterogeneous Catalysis Using MCM-41 Type Silicas Functionalized with Amino Groups. Journal of Organic Chemistry, 1997, 62, 749-751.
54. Shephard D. S., Zhou W., Maschmeyer T., Matters J. M., Roper C. L., Parsons S., Johnson B. F. G., Duer M. J.. Site-Directed Surface Derivatization of MCM-41: Use of High-Resolution Transmission Electron Microscopy and Molecular Recognition for Determining the Position of Functionality within Mesoporous Materials. Angewandte Chemie International Edition, 1998, 37, 2719-2723.
55. Lasperas M., Llorett T., Chaves L., Rodriguez I., Cauvel A., Brunel D.. Heterogeneous Catalysis and Fine Chemicals, Elsevier Science: New York, 1997, Vol. Iv, p 75.
56. Angeletti E., Canepa C., Martinetti G., Venturello P.. Silica Gel Functionalized with Amino Groups as a New Catalyst for Knoevenagel Condensation under Heterogeneous Catalysis Conditions. Tetrahedron Letters, 1988, 29, 2261-2264.
57. Mercier L., Pinnavaia T. J.. Direct Synthesis of Hybrid Organic-Inorganic Nanoporous Silica by a Neutral Amine Assembly Route: Structure-Function Control by Stoichiometric Incorporation of Organosiloxane Molecules. Chemistry of Materials, 2000, 12, 188-196.
58. Jaroniec M., Kruk M., Jaroniec C. P.. Modification of Surface and Structural Properties of Ordered Mesoporous Silicates. Adsorption, 1999, 5, 39-45.

59. Burwell R. L. Jr., Leal O.. Modified Silica Gels as Selective Adsorbents for Sulfur Dioxide. Chemical Communications, 1974, 342.

60. Angeletti E., Canepa C., Martinetti G., Venturello P.. Amino Groups Immobilized on Silica Gel: An Efficient and Reusable Heterogeneous Catalyst for the Knoevenagel Condensation. Journal of the Chemical Society, Perkin Transactions I, 1989, 105-107.

61. Zhao X. S., Lu G. Q.. Modification of MCM-41 by Surface Silylation with Trimethylchlorosilane and Adsorption Study. Journal of Physical Chemistry B, 1998, 102, 1556-1561.

62. Harlick P. J. E., Sayari A.. Applications of Pore-Expanded Mesoporous Silica. 5. Triamine Grafted Material with Exceptional CO_2 Dynamic and Equilibrium Adsorption Performance. Industrial & Engineering Chemistry Research, 2007, 46, 446-458.

63. Khatri R. A., Chuang S. S. C., Soong Y., Gray M.. Carbon Dioxide Capture by Diamine-Grafted SBA-15: A Combined Fourier Transform Infrared and Mass Spectrometry Study. Industrial & Engineering Chemistry Research, 2005, 44, 3702-3708.

64. Hook R.J.. An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds. Industrial & Engineering Chemistry Research, 1997, 36, 1779-1790.

65. Gregory P. Knowles, Graham J. V., Delaney S. W., Chaffee A. L.. Aminopropyl-functionalized Mesoporous Silicas as CO_2 Adsorbents. Fuel Processing Technology, 2005, 86, 1435-1448.

66. Cussler E. L., Moggridge G. D.. Chemical Product Design. Cambridge University Press: New York, 2001.

67. Maccabe W. J., Smith J. C., Harriott P.. Unit Operations of Chemical Engineering, 4th ed.. McGraw-Hill: New York, 1985.
68. Fogler H. S.. Elements of Chemical Reaction Engineering, 3rd ed.. Prentice Hall: Englewood Cliffs, NJ, 1999.
69. Feng X., Fryxell G. E., Wang L. Q., Kim A. Y., Liu J., Kemner K. M.. Functionalized Monolayers on Ordered Mesoporous Supports. Sciesnce, 276 (5314): 923-926.
70. Hiyoshi N., Yogo K., Yashima T.. Adsorption of Carbon Dioxide on Amine Modified SBA-15 in the Presence of Water Vapor. Chemistry Letters, 2004, 33, 510-511.
71. Knowles G. P., Delaney S. W., Chaffee A. L.. Amine-Functionalised Mesoporous Silicas as CO_2 Adsorbents. Studies in Surface Science and Catalysis, 2005, 156, 887-896.
72. Knowles G. P., Delaney S. W., Chaffee A. L.. Diethylenetriamine[propyl(silyl)]-Functionalized (DT) Mesoporous Silicas as CO_2 Adsorbents. Industrial & Engineering Chemistry Research (2006), 45(8), 2626-2633.
73. Harlick P. J. E., Sayari A.. Applications of Pore-Expanded Mesoporous Silica. 3. Triamine Grafted Material with Exceptional CO_2 Dynamic and Equilibrium Adsorption Performance. Industrial & Engineering Chemistry Research, 2006, 45, 3248-3255.
74. Zheng F., Tran D. N., Busche B. J., Fryxell G. E., Addleman R. S., Zemanian T. S., Aardahl C. L.. Ethylenediamine-Modified SBA-15 as Regenerable CO_2 Sorbent. Industrial & Engineering Chemistry Research, 2005, 44, 3099-3105.
75. Franchi R., Harlick P. J. E., Sayari A.. Applications of Pore-Expanded Mesoporous Silica. 2. Development of a High-Capacity, Water-Tolerant Adsorbent for CO_2. Industrial & Engineering Chemistry Research, 2005, 44, 8007-8013.

76. Huang L. M., Wang H. T., Chen J. X., Wang Z. B., Sun J. Y., Zhao D. Y., Yan Y. S.. Synthesis, Morphology Control, and Properties of Porous Metal–organic Coordination Polymers. Microporous & Mesoporous Materials, 2003, 28, 105-114.
77. Zhao Z. X., Li Z., Lin Y. S.. Adsorption and Diffusion of Carbon Dioxide on Metal−Organic Framework (MOF-5). Industrial & Engineering Chemistry Research, 2009, 48, 10015–10020.
78. Millward A. R., Yaghi O. M.. Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. Journal of the American Chemical Society, 2005, 127, 17998–17999.
79. F_erey G., Mellot-Draznieks C., Serre C., Millange F., Dutour J., Surbl_e S., Margiolaki I.. A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. Science, 2005, 309, 2040–2042.
80. Chowdhury, P.; Bikkina, C.; Gumma, S. Gas Adsorption Properties of the Chromium-Based Metal Organic Framework MIL-101. Journal of Physical Chemistry C, 2009, 113, 6616–6621.
81. Hong D.-Y., Hwang Y. K.,; Serre C., F_erey G., Chang J.-S.. Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites: Surface Functionalization, Encapsulation, Sorption and Catalysis. Advanced Functional Material, 2009, 19, 1537–1552.
82. Jhung S. H., Lee J. H., Yoon J. W., Serre C., Ferey G., Chang J. S.. Microwave Synthesis of Chromium Terephthalate MIL-101 and Its Benzene Sorption Ability. Advanced Materials, 2007, 19, 121–124.

83. Maksimchuk N. V., Timofeeva M. N., Melgunov M. S., Shmakov A. N., Chesalov Y. A., Dybtsevb D. N., Fedinb V. P., Kholdeeva O. A.. Heterogeneous Selective Oxidation Catalysts Based on Coordination Polymer MIL-101 and Transition Metal-substituted Polyoxometalates. Journal of Catalysis, 2008, 257, 315–323.

84. Liu Y. Y., Zeng J. L., Zhang J., Xu F., Sun L. X.. Improved Hydrogen Storage in the Modified Metal-organic Frameworks by Hydrogen Spillover Effect. Int. J. Hydrogen Energy, 2007, 32, 4005–4010.

85. Zhao X. X., Xu, X. L., Sun L. B., Zhang L. L., Liu X. Q.. Adsorption Behavior of Carbon Dioxide and Methane on $AlPO_4$-14: A Neutral Molecular Sieve. Energy & Fuels, 2009, 23, 1534-1538.

86. Liang Z., Marshall M., Chaffee A. L.. CO_2 Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X). Energy & Fuels 2009, 23, 2785-2789.

87. Hyun S. H., Danner R. P.. Equilibrium Adsorption of Ethane, Ethylene, Isobutane, Carbon Dioxide, and Their Binary Mixtures on 13X Molecular Sieves. Journal of Chemical and Engineering Data, 1982, 27, 196-200.

88. Tanthana J., Chuang S. S. C.. In Situ Infrared Study of the Role of PEG in Stabilizing Silica-supported Amines for CO_2 Capture. ChemSusChem, 3, 957-964.

89. Jentys A., Kleestorfer K., Vinek H.. Concentration of Surface Hydroxyl Groups on MCM-41. Microporous Mesoporous Materials, 1999, 27, 321-328.

90. Landmesser H., Kosslick H., Storek W., Fricke R.. Interior Surface Hydroxyl Groups in Ordered Mesoporous Silicates. Solid State Ionics, 1997, 101-103, 271-277.

91. Takei T., Kato K., Meguro A., Chikazawa M.. Infrared Spectra of Geminal and Novel Triple Hydroxyl Groups on Silica Surface. Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 1999, 150, 77-84.
92. Zhao X. S., Lu G. Q., Whittaker A. K., Millar G. J., Zhu H. Y.. Comprehensive Study of Surface Chemistry of MCM-41Using ^{29}Si CP/MAS NMR, FTIR, Pyridine-TPD, and TGA. Journal of Physical Chemistry B, 1997, 101, 6525.
93. Danckwert P. V.. The Reaction of CO_2 with Ethanolamines. Chemical Engineering Science, 1979, 34, 443-446.
94. Stein A.. Advances in Microporous and Mesoporous Solids - Highlights of Recent Progress. Advanced Materials, 2003, 15, 763-775.
95. Sayari A.. Unprecedented Expansion of the Pore Size and Volume of Periodic Mesoporous Silica. Angew. Chem. Int. Ed. Engl., 2000, 39, 2920-2922.
96. http://www.epa.gov/cleanenergy/energy-and-you/affect/coal.html.
97. Gray M. L., Champagne K. J., Fauth D. F., Baltrus J. P., Pennline H.. Performance of Immobilized Tertiary Amine Solid Sorbents for the Capture of Carbon Dioxide. International Journal of Greenhouse Gas Control, 2008, 2, 3-8.
98. http://www.che.utexas.edu/course/che359&384/lecture_notes/topic_3/Chapter9.pdf.
99. Linak W. P., Peterson T. W.. Effect of Coal Type and Residence Time on the Submicron Aerosol Distribution from Pulverized Coal Combustion. Aerosol Science and Technology, 1984, 3, 77-96.
100. Jin H., Ishida M.. A Novel Gas Turbine Cycle with Hydrogen-fueled Chemical-looping Combustion. International Journal of Hydrogen Energy, 2000, 25, 1209-1215.

APPENDIX

In estimating the size of CO_2 capture unit of a power plant, the following assumptions were made.

1. 500MW power capacity from a coal-fired power plant
2. CO_2 emission rate of 2249 lb/MWh [96]
3. CO_2 adsorption capacity of 3.5 mmol/g sorbent [97]
4. The density of the sorbent of 0.3 g/cm^3 [2]
5. A mean gas residence time of 2 seconds was assumed for complete combustion in the pulverized coal boiler [98, 99]
6. CO_2 adsorption in the adsorber of 5 minutes [88]
7. The sorbent was filled within 1/3 of the volume of the adsorber
8. The desorber had the same size as the adsorber [88]

Based on the above assumptions the size of CO_2 adsorption and desorption units was estimated to be approximately 2760 m^3 for both. See the Mathcad calculation on the next page.

$$\mathrm{mmol} \equiv 0.001\mathrm{mol}$$

CO_2 emission rate from coal-fired power plant in US

$$R\_CO2 := 2249\,\frac{\mathrm{lb}}{\mathrm{MW}\cdot\mathrm{hr}}$$

Assume a coal-fired power plant with a capacity of 500 MW

$$Capacity\_power := 500\mathrm{MW}$$

The mass of CO_2 generated in one second is:

$$m\_CO2 := R\_CO2\cdot Capacity\_power\cdot 1\mathrm{s} = 141.685\,\mathrm{kg}$$

Molecular mass of CO_2 is: $M\_CO2 := 44\,\frac{\mathrm{gm}}{\mathrm{mol}}$

The amount of CO_2 generated in one second is:

$$n\_CO2 := \frac{m\_CO2}{M\_CO2} = 3.22\times 10^{3}\,\mathrm{mol}$$

Assume the power plant is using a sorbent whose CO_2 adsorption capacity is:

$$CO2\_capacity := 3.5\cdot\frac{\mathrm{mmol}}{\mathrm{gm}}$$

The mean gas residence time in a pulverized coal boiler is about 2 seconds.

$$t\_boiler := 2\mathrm{s}$$

Assume the CO_2 adsorption takes time of 5 minutes

$$t\_adsorption := 5\mathrm{min}$$

The ratio of the CO_2 adsorption time to gas residence time in the boiler is:

$$r := \frac{t\_adsorption}{t\_boiler} = 150$$

The mass rate of sorbent for CO_2 capture from the power plant is

$$m\_sorbent := \frac{n\_CO2}{CO2\_capacity}\cdot r = 1.38\times 10^{5}\,\mathrm{kg}$$

Assume the density of the sorbent is:

$$\rho\_sorbent := 0.3\,\frac{gm}{cm^3}$$

The volume of the sorbent is:

$$V\_sorbent := \frac{m\_sorbent}{\rho\_sorbent} = 4.6 \times 10^5\,L$$

Assume the sorbent occupies 1/3 of the adsorber, the volume of the reactor is:

$$V\_adsorber := 3 \cdot V\_sorbent = 1.38 \times 10^3\,m^3$$

Assume the desorber has the same size as the adsorber

$$V\_desorber := 1 \cdot V\_adsorber = 1.38 \times 10^3\,m^3$$

The size of the CO_2 adsorption/desorption sector of the power plant is:

$$V\_sorber := V\_adsorber + V\_desorber = 2.76 \times 10^3\,m^3$$

VITA

Bingyu Li, born in China, graduated from Zhejiang University, China with a Bachelor of Science in Thermal Energy and Power Engineering in 2004, and obtained a Master of Science in Engineering Thermophysics from Chinese Academy of Sciences, China in 2007. She enrolled at the University of Mississippi in the fall of 2009 to pursue graduate studies in the Department of Chemical Engineering, focusing in the area of carbon dioxide capture. And she plans to work as an engineer in the industry in the future.