#### United Arab Emirates University Scholarworks@UAEU

Theses

**Electronic Theses and Dissertations** 

2009

# Carbon dioxide capture from Flue gases

Mohamed Rashid Al Rashid

Follow this and additional works at: https://scholarworks.uaeu.ac.ae/all\_theses Part of the <u>Petroleum Engineering Commons</u>

**Recommended** Citation

Al Rashid, Mohamed Rashid, "Carbon dioxide capture from Flue gases" (2009). *Theses*. 348. https://scholarworks.uaeu.ac.ae/all\_theses/348

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Scholarworks@UAEU. It has been accepted for inclusion in Theses by an authorized administrator of Scholarworks@UAEU. For more information, please contact fadl.musa@uaeu.ac.ae.



United Arab Emirates University Deanship of Graduate Studies M.Sc. Program in Petroleum Science and Engineering

# **CARBON DIOXIDE CAPTURE FROM**

## **FLUE GASES**

By

### **Mohamed Rashid Al Rashid**

A Thesis submitted to United Arab Emirates University in partial fulfillment of the requirements for the degree of M.Sc. in Petroleum Science & Engineering

2009



United Arab Emirates University Deanship of Graduate Studies M.Sc. Program in Petroleum Science and Engineering

#### Thesis Title

Carbon Dioxide Capture from Flue Gases

Authors Name

Mohamed Rashid AL-Rashid

#### Supervisor

No.	Name	Position
1	Dr. Nayef Ghassem	Associate Professor of Chemical Engineering





2487 3 1

where we have a

Carbon Dioxide Capture from Flue Gases Thesis of Mohamed Rashid Al Rashid Submitted in Partial Fulfillment for the Degree of Master of Petroleum Science and Engineering (Chemical Engineering)

Chair of Examination Committee Nayef Mohamed Ghasem Chemical & Petroleum Engineering Department United Arab Emirates University

External Examiner Prof. Tariq Al-Fariss Department of Chemical Engineering King Saud University

Internal Examiner Prof. Kamal Mustafa Department of Mechanical Engineering United Arab Emirates University

Associate Dean of Research & Graduate Studies Dr. Ali Al-Marzouqi ----

United Arab Emirates University 2008/2009

#### Acknowledgement

I would like to express my deep gratitude and thanks to my thesis supervisor Dr. Nayef Ghasem for his valuable comments and suggestion. I would also like to thank the master program coordinator, Prof. Dr. Abdul Razak Zekri, for his kindness, encouragement and continuous support during the period of my study. Special thanks to Prof. Kamal Mustafa and Prof. Tariq F. Al Fariss for agreeing to serve in my thesis examination Committee. I would also like to thank the team engineers of FERTIL for supplying industrial data and valuable comments.

#### Abstract

Global warming and climate change are believed to be caused by the greenhouse effect. CO2 has been regarded as the main contributor to global climate change which directly results in serious environmental problems. Half of the anthropogenic CO<sub>2</sub> emission sources are emitted from the combustion of fossil fuels in industries and power plants world-wide. The absorption behavior of carbon dioxide from flue gases can be studied using conventional absorber and polymeric hollow fiber membrane contactors. An Industrial absorber data was compared with simulated data using hollow fiber membrane contactor using the gPROMs software package. In this analysis, with the absorbent solution flowing in the inner side of the fiber bore and the pure gas in the shell, the module was operated in a non-wetted mode. The derived coupled, non-linear partial differential equations were solved by the backward finite difference method. The Diethanolamine (DEA) was used as absorbent. The outlet absorbed carbon dioxide concentration was simulated and studied with respect to the liquid velocity, initial amine concentration and external mass transfer coefficient. The analysis includes the effects of the diameter and length of the fibers on the liquid outlet gas concentration as a function of the liquid velocity in the fiber. It was found that the liquid velocity and initial absorbent concentrations, as well as the fiber inner diameter and length, have a tremendous effect on the carbon dioxide removal performance.

# **TABLE OF CONTENTS**

Abstract	iii
1. Chapter 1	
Introduction	1
1.1 Carbon Dioxide Capture and Storage	1
1.2 Carbon Dioxide Emission	2
1.3 Carbon Dioxide Capture and Storage Processes	3
1.4 Capturing CO <sub>2</sub>	4
1.5 CO <sub>2</sub> Capture Sources	5
1.5.1 CO <sub>2</sub> Capture in Manufacturing Industry	6
1.5.2 CO <sub>2</sub> Capture in Fuel Supply	
1.6 CO <sub>2</sub> Transportation	12
1.7 CO <sub>2</sub> Storage	13
1.7.1 CO <sub>2</sub> Enhanced oil recovery	14
1.7.2 CO <sub>2</sub> Enhanced gas recovery	15
1.7.3 CO <sub>2</sub> coal bed methane recovery	15
1.7.4 Depleted oil & gas fields	17

1.7.5 Storage in deep saline aquifers	17
1.7.6 Other storage options	19
1.8 CO2 capture using hollow fiber membrane contactor	22
2. Chapter 2	
Modeling & Simulation	26
3. Chapter 3	
Results & Discussion	32
3.1 Conventional Industrial Absorber	32
3.2 Polymeric hollow fiber membrane	38
Conclusion	44
References	45

### List of Tables

Table No.	Table Name	Page
1	Overview of CCS projects	4
2	Comparison with conventional MEA process	22
3	Effect of pressure	33
4	Effect of temperature	34
5	Effect of flue gas rates	35
6	Effect of solvent flow rates	37
7	specifications of HF contactors	38

# List of Figures

Figure No.	Figure Name	Page
1	Carbon dioxide capture schematic	23
2	Pressure vs. CO <sub>2</sub> recovery graph	34
3	Temperature vs. CO <sub>2</sub> recovery graph	35
4	Gas flow rate vs. CO <sub>2</sub> recovery graph	36
5	Solvent flow vs. CO <sub>2</sub> recovery graph	37
6	Dimensionless CO <sub>2</sub> & DEA concentration profile	39
7	CO <sub>2</sub> concentration profile for membrane radius	40
8	DEA concentration profile for membrane radius	41
9	Effect of liquid velocity on amine concentration	42
10	Effect of liquid velocity on CO2 concentration	43
11	Effect of amine concentration on CO <sub>2</sub> depletion	44

vii

### Nomenclature

AT	total surface area of gas liquid contact, m <sup>2</sup>
$A_{i,j}$	matrix coefficients of the weight first derivative
$B_{ij}$	matrix coefficients of the weight second derivative
Ċт	total amine concentration, mol/m <sup>3</sup>
di	inner fiber diameter, m
d <sub>lm</sub>	logarithmic mean average diameter
do	outer fiber diameter, m
$\mathrm{D}_{Ag}$	diffusion coefficient of specie CO <sub>2</sub> in air, m <sup>2</sup> /s
D <sub>AK</sub>	continuum Knudsen diffusion coefficient of specie CO <sub>2</sub> , m <sup>2</sup> /s
E	dimensionless enhancement factor
Gr	dimensionless Graetz number
Н	dimensionless Henry's law constant, dimensionless
k <sub>Ag</sub>	gas film mass transfer coefficient of specie A, m/s
<b>k</b> AI	liquid film mass transfer coefficient of specie A, m/s
k <sub>Am</sub>	membrane mass transfer coefficient of specie A, m/s
$k_{Bi}$	forward second order reaction rate constant,
kov	overall reaction rate constant, m/s
kz	forward second order reaction rate constant
k_z	reverse second order reaction rate constant
Keq	equilibrium constant
Kext	external mass transfer coefficient, m/s
Kov	overall mass transfer coefficient, m/s
l	active membrane fiber length, m
m	distribution coefficient, dimensionless
m	partition coefficient between gas and liquid phase, dimensionless
$M_i$	molecular weight of specie i, kg/mol
n	number of fiber in the bundle, dimensionless
r	radial coordinate
Γi	inner fiber radius

viii

- r<sub>o</sub> outer fiber radius, m
- Sh dimensionless Sherwood number, K<sub>cxt</sub>d/D, dimensionless
- T temperature in K
- z axial contactor coordinate

#### Greek letters

ς	dimensionless axial coordinate
δ	membrane thickness
η	extent of gas removal
ξ	dimensionless radial coordinate
ξi	collocation point
$\Phi_{\rm il}$	dimensionless concentration of specie <i>i</i> in the liquid phase
$\Phi_{\rm ili}$	dimensionless inlet concentration of specie <i>i</i> in the liquid phase
$\Phi_{ilo}$	dimensionless outlet concentration of specie <i>i</i> in the liquid phase
τ	membrane's pore tortuosity

ix



#### Chapter 1

#### Introduction

#### 1.1 Carbon dioxide capture and storage

Meeting the world's growing demand for affordable, secure and convenient energy while reducing GHG emissions - particularly CO2 - is the energy challenge faced today. GHG emissions need to be cut by 50-80% by 2050, in order to avoid the devastating consequences of climate change (IPCC, 2007). In the International Energy Outlook 2007, the IEA predicted a total CO<sub>2</sub> emission reduction of 32 Gt by 2050, using various technology options in different sectors. The results show that end-use efficiency could contribute up to 45% reduction, whereas the next major reduction would come from carbon capture and storage (CCS) technologies, which would contribute up to 20% reduction (Figure 1). If done responsibly, CCS could be a safe and important way to mitigate the increasing emissions. Approximately an additional 230 Gt of additional CO<sub>2</sub> will be in the atmosphere by 2050, if CCS is not used. In addition to being stored underground, CO<sub>2</sub> can be used for Enhanced Oil Recovery (EOR) and other applications, such as mineralization and cooling. Carbon capture and storage (CCS) technologies are based on capturing carbon dioxide (CO<sub>2</sub>) from large point sources such as fossil fuel power plants. Currently, CCS is gaining attention as an option for reducing CO<sub>2</sub> emissions, and covers a broad range of technologies that are being developed to allow carbon dioxide (CO<sub>2</sub>) emissions from fossil fuel usage at large point sources to be transported to safe geological storage. instead of releasing it into the atmosphere. Currently, fossil fuels are being used extensively and therefore, if no new policies are put in place, CO2 emissions will rise over the next half century. It is clear that such development is not

sustainable. There are a number of existing options that can reduce the CO<sub>2</sub> emissions from the energy system. These include improved energy efficiency and a switch to renewable and nuclear energy. However, policies based on these options will, at best, only partly solve the problem. Carbon dioxide capture and storage (CCS) technologies constitute another promising option that can drastically reduce these emissions. Accomplishing this would require governments taking immediate action ensuring that CCS technologies are developed and deployed on a large scale over the next few decades. However, the potential benefits of CCS can be further illustrated by comparing the emission with, and without, CCS. The emission levels in 2050 would increase by over a quarter compared to the case in which CCS was included [1].

#### 1.2 CO<sub>2</sub> Emission

The world's dependence on fossil fuels for the satisfaction of primary energy needs cause increasing atmospheric emissions of  $CO_2$  from the combustion of hydrocarbons. For the coming decades, fossil fuels will continue to provide more than 80% of the total world energy requirements, especially with coal and natural gas asserting their positions in the fuel mix to 38% and 30%, respectively, of electricity demand in 2030. On a global basis, in 2004, the primary energy consumption for coal accounted for 24%, and for oil 34%, for natural gas 21%, for nuclear 5%, for large hydropower 6% and renewable accounting for approximately 10%. Power generation accounted for the largest source of  $CO_2$  emissions.

Moreover, as fossil fuel based heat and power production counted as sources of  $CO_2$  emission, there are also other large stationary sources of  $CO_2$  emissions, such as natural gas sweetening, hydrogen production for ammonia and ethylene oxide, oil refineries, iron and steel production facilities, cement and limestone manufacturing plants. As these sources

increase, the effects of  $CO_2$  in the environment will also increase and consequently, the environment will continue to suffer serious problems because of the increase in  $CO_2$ emissions. The concentration of  $CO_2$  in the Earth's atmosphere has increased during the past century. Currently, 4 (Gt C) of carbon per year increases in the atmosphere. The total human industrial magnitude of  $CO_2$  production from using coal, oil, natural gas and the production of cement, is currently about 8 Gt C per year. Moreover, humans exhale about 0.6 Gt C per year, which has been sequestered by plants from atmospheric  $CO_2$ . The concentration of  $CO_2$ in the air exceeds 1,000 ppm  $CO_2$  [2].

In general, the global  $CO_2$  emissions increased by 70% between 1971 and 2002. Since 1990  $CO_2$  emissions have risen by 16% (see figure 1.1). The Reference Scenario of the IEA World Energy Outlook (WEO) projects that global emissions will be up 63% on today's level by 2030, around 90% higher than 1990 levels. Historically,  $CO_2$  emissions have come overwhelmingly from industrialized countries. However, two thirds of the increase up to 2030 is expected to come from developing countries. By 2030, developing nations are set to account for almost 49% of global  $CO_2$  emissions (up from 35% today), with Organization for Economic Co-operation and Development (OECD) countries accounting for 42% and transition economies for 9%. The estimation of  $CO_2$  emission through the past three decades was as follows: burning of coal caused an increase in global  $CO_2$  emissions by 40%, oil is responsible for 31% and gas 29% [3].

#### **1.3** CO<sub>2</sub> Capture and Storage CCS Processes

 $CO_2$  Capture and Storage (CCS) include three distinct processes, first; capturing  $CO_2$  from the gas streams emitted during electricity production, industrial processes or fuel processing;

second, transporting the captured  $CO_2$  by pipeline or in tankers; and third, storing  $CO_2$ underground in deep saline aquifers, depleted oil and gas reservoirs. These three processes have been in use for decades. Moreover, the table below provides an overview of CCS projects.

#### Table 1: Overview of worldwide CCS projects

CCS projects	Number of projects
CO <sub>2</sub> capture demonstration projects	11
CO <sub>2</sub> capture R&D projects	35
Geologic storage projects	26
Geologic storage R&D projects	74
Ocean storage R&D projects	9

There are many small-scale pilot plants based on new capture technologies are in operation around the world.

#### 1.4 Capturing CO<sub>2</sub>

By using the new, existing and the emerging technologies,  $CO_2$  can be captured either before or after combustion. In conventional processes,  $CO_2$  is captured from the flue gases produced during combustion (post-combustion capture) and it is also possible to convert the hydrocarbon fuel into  $CO_2$  and hydrogen by removing the  $CO_2$  from the fuel gas and combust the hydrogen (pre-combustion capture).

The pre-combustion depends on the physical absorption of CO<sub>2</sub> and it is the most promising capture option, while in post-combustion capture, options include processes based

on chemical absorption or oxyfueling (combustion using oxygen separated from air, which generates nearly pure CO<sub>2</sub> flue gas). Both pre-combustion and post-combustion capture can use the technology of longer-term, gas separation membranes and other new technologies. In fact, the success of a CCS strategy depends on the use of plants. For coal-fired plants, Integrated Gasification Combined Cycle (IGCC) fitted with physical absorption technology is used to capture CO<sub>2</sub> at the pre-combustion stage. For coal-fired Ultra Supercritical Steam Cycles (USCSC) fitted with post-combustion capture technologies or various types of oxyfueling technology (including chemical looping, where the oxygen is supplied through a chemical reaction), may emerge as alternatives. For natural gas-fired plants, use of the strategy of oxyfueling (including chemical looping), pre-combustion gas shifting and physical absorption in combination with hydrogen turbines, or post-combustion chemical absorption are promising options. For the later stage, fuel cells are expected to integrate into high-efficiency coal and gas-fired power plants fitted with CCS.

#### 1.5 CO<sub>2</sub> Capture Sources

 $CO_2$  can be captured from all installations used to combust fossil fuels and biomass, provided that the scale of the emissions source is large enough. In practice, there are only three areas suitable: The first source is electricity generation (including district heating and industrial combined heat and power generation) which would be responsible for 29% of total current  $CO_2$  emissions and capturing  $CO_2$  from coal, natural gas, oil and biomass-fired power plants. The second source is industrial processes from which  $CO_2$  can be captured from the production processes of iron, cement, chemicals and pulp, activities which generate a combined 23% of world  $CO_2$  emissions. It was noticed that the cost of applying CCS in industry is lower than for power generation and in other cases it is similar. Finally, fuels processing where  $CO_2$  can be captured from oil refineries, natural gas processing installations and synfuel production. Also, there are other sources of emissions such as from the transport, agriculture, service and residential sectors but are too dispersed to make capture viable.

#### 1.5.1 CO<sub>2</sub> Capture in the Manufacturing Industry

 $CO_2$  capture could be applied in many production processes in the manufacturing industry. Industrial sources of relatively pure  $CO_2$  are the production of ammonia, ethylene oxide, existing hydrogen production and production of direct reduced iron (DRI). However, a number of important industrial processes such as blast furnaces, cement kilns and steam crackers are characterized by lower  $CO_2$  concentrations but with large quantities of  $CO_2$ , but because of the low concentrations of  $CO_2$ , they would require either costly and energyintensive  $CO_2$  chemical absorption processes, or process re-design to increase  $CO_2$ concentrations, such as those based on the use of oxygen in combination with postcombustion  $CO_2$  removal or hydrogen production in combination with pre-combustion  $CO_2$ removal [4].

#### 1.5.1.1 Ammonia Production

Nitrogen fertilizers are produced from ammonia, which is produced from hydrogen. The hydrogen is produced from natural gas, heavy oil or coal. In the old ammonia production plants,  $CO_2$  was separated from the hydrogen before the ammonia production step, while in new plants, hydrogen, rather than  $CO_2$ , is separated from the syngas. The remaining gas containing  $CO_2$ , CO, unconverted methane, etc., is used as a fuel in the reformer furnace. In this case, there is no pure  $CO_2$  stream, if there was a need to produce pure  $CO_2$  it would be

switched back to the old plant design. The separated  $CO_2$  is used for the production of urea (CH<sub>4</sub>N<sub>2</sub>O), a popular type of nitrogen fertilizer and 0.88 tons of CO<sub>2</sub> are needed for each tone of urea produced. The Energy use for ammonia production amounts to 25-40 GJ/t, resulting 1.5 tons CO<sub>2</sub> emission per ton of ammonia.

#### 1.5.1.2 Iron and Steel Production

The amounts of  $CO_2$  are captured in the iron and steel industry in the production of Direct Reduced Iron (DRI) and the  $CO_2$  is released into the atmosphere. Global DRI production amounted to 38 Mt in 2001, which caused about 20-30 Mt  $CO_2$  emissions. The production of DRI is mostly concentrated in countries with cheap stranded gas, including the Middle East. Iron production in blast furnaces needs about 500-550 kg of coke and coal per ton of product and the amount of iron production is approximately 540 Mt, which provides a source of around 1,000 Mt of  $CO_2$ . As secondary steel production grows, the iron production is planned to be around 350-400 Mt in 2030. The  $CO_2$  emissions from blast furnaces amounts to 1-1.5 t/t iron and this  $CO_2$  can be removed by re-designing the blast furnace for oxygen use and, subsequently, removing  $CO_2$  using physical absorbents but this strategy has received limited attention. Additionally, if  $CO_2$  capture was applied to iron and steel production, its potential would be in the order of 0.5-1.5 Gt per year.

#### 1.5.1.3 Cement

Worldwide, cement kilns produce about 1.3 Gt  $CO_2$  per year, equal to 0.6-1.0 t  $CO_2$  per tonne of Portland cement, depending on fuel and energy efficiency. As the cement production is increasing,  $CO_2$  emissions from this source category are rising. In the off-gases,  $CO_2$  concentrations are higher than for conventional furnaces in other sectors, because more than half of the  $CO_2$  in off-gas which comes from a chemical reaction for cement production (so-called calcinations):

 $CaCO_2 \rightarrow CaO + CO_2$ 

Energy-related  $CO_2$  emissions depend on the energy efficiency of the kiln (which may range from 3-8 GJ/t cement clinker) and on fuel type (more than half of the fuel may be waste wood, waste tires etc., which is often not properly accounted for in energy statistics). Currently, no radically new designs have been proposed for cement kilns. The capture technology could be similar to that of an Integrated Gasification Combined Cycle (IGCC) or a pulverised coal fired power plant with  $CO_2$  capture from the flue gas. It might be possible to use oxygen instead of air in cement kilns.

#### 1.5.2 CO<sub>2</sub> Capture in Fuel Supply

The extraction of oil, gas and coal results in almost 400 Mt of  $CO_2$  emissions. The most important emissions source is the fuel transformation sector. Petroleum refineries and Liquefied Petroleum Gas production (LNG) result for 700 Mt of  $CO_2$  emissions per year. In future, these emissions are expected to increase significantly. On the fuels supply, the LNG production will increase as a result of larger quantities of natural gas being transported over longer distances, where pipelines do not account for as a proper alternative. Presently, emissions from oil products used exceed the emissions from oil production and processing to a considerable extent. However, synfuel production (e.g., through Fischer-Tropsch synthesis) is more energy intensive than conventional refining. Using hydrogen as a transportation fuel can produce e zero vehicle tailpipe emissions, and has significant potential to capture  $CO_2$ from hydrogen production. Synfuels are expected to gain an increasing market share. Synfuels such as hydrogen, methanol, dimethylether, synthetic gasoline and diesel can be produced from natural gas, coal or biomass, and  $CO_2$  capture could be applied to these production processes. There are four categories of  $CO_2$  capture from fuel supply:

- CO<sub>2</sub> capture in natural gas processing;
- Refinery CO<sub>2</sub> capture;
- Hydrogen production processes;
- Gasification and Fischer-Tropsch production of synfuels.

#### 1.5.2.1 Natural Gas Processing

The CO<sub>2</sub> content of natural gas varies from virtually zero in Siberian gas, to 1.5% in certain North Sea gas fields, and up to 70% in fields such as Natuna in Indonesia. The latter value is an extreme; an average CO<sub>2</sub> content is 1-2%. The magnitude of CO<sub>2</sub> that is released when the gas is combusted is larger than the CO<sub>2</sub> from gas processing, and this will limit the worldwide potential for CO<sub>2</sub> capture in natural gas processing to less than 100 Mt CO<sub>2</sub> capture per year. The CCS for natural gas processing is getting more attention because the process is expensive and the additional cost is limited for compression, transportation and storage. CO<sub>2</sub> should be captured before the gas can be sold, as storage sites are often nearby. Moreover, CO<sub>2</sub> storage wells are similar to gas production wells, so the necessary equipment and expertise are available on site. At this time, most existing and planned CCS projects are gas production projects, such as the Sleipner and Snohvit projects in Norway, Salah project in Algeria, Gorgon project in Australia and the Natuna project in Indonesia.

#### 1.5.2.2 Oil Refineries

Oil refineries are processes to convert crude oil into oil products. They do refining through a wide range of process operations, such as distillation, reforming, hydrogenation and cracking. While distillation processes require low temperature heat; hydrogenation requires hydrogen, and cracking produces heat and  $CO_2$  from heavy oil residues. Also, refineries consume significant amounts of electricity. Reformers, fluid catalytic crackers (FCCs) and possibly vacuum distillation units could be equipped with high-temperature CHP units with  $CO_2$  capture and they represent 30-40% of the refinery energy consumption. Currently, refineries have higher emissions than that because they use heavier crude and produce more light products, especially gasoline and diesel. Refinery heaters can be equipped with post-combustion  $CO_2$  capture technology. A study for a UK refinery and petrochemical complex suggests that collecting 2 Mt of  $CO_2$  per year would require 10 MW for blowers to push the flue gas through the network, and 10 MW for the pressure drop imposed by the packed column absorbers which equals 0.39 GJ/t  $CO_2$ .

To reduce the concentration of NOx and SO<sub>2</sub>, pre-treatment is required and the system needs about 396 MW of natural gas, which amounts to 6.2 GJ of natural gas per tone of CO<sub>2</sub> captured. This includes the energy needs for the blowers and the steam for the regeneration of absorbents. This is a fairly high energy consumption; compared to CO<sub>2</sub> capture energy requirements for power plants. The product mix of refineries is changing towards more light products with a higher H/C ratio, as demand growth is concentrated in transportation markets. The refineries can respond to hydrogen deficiency by adding hydrogen (a process called hydro cracking) or by removing carbon (a process called coking).

#### 1.5.2.3 Hydrogen Production

Hydrogen is a  $CO_2$ -free energy carrier. When hydrogen is produced from carbon-containing energy carriers,  $CO_2$  and hydrogen should be separated to produce pure hydrogen. The first step strategy toward a hydrogen economy could be hydrogen production from fossil fuels, with  $CO_2$  capture, followed by hydrogen production from other  $CO_2$ -free primary energy sources in the longer term. In the future, hydrogen is widely expected to be the transportation fuel. The competitiveness of hydrogen as a transportation fuel critically depends on the cost of hydrogen vehicles and the efficiency gains compared to conventional vehicle engines.

All production routes that involve electrolysis are considerably more expensive: the two-step approach of electricity production, followed by hydrogen production, incurs higher capital costs, and reduces efficiency and this could be a hurdle for any hydrogen economy built on renewable *resources*, except biomass and concentrated solar heat, since they would not involve electrolysis. While exploring whether technology can reduce the cost of hydrogen production from renewables, its cost will remain prohibitive in all, but a few regions with abundant cheap renewable energy, such as Iceland.

Hydrogen production from biomass is a strategy that reduces atmospheric CO<sub>2</sub> concentrations and produces energy at the same time. The scale of biomass hydrogen production is typically smaller than coal-based hydrogen production. Given that investment costs of chemical plants typically increase with a scale factor of 0.7, the specific investment costs for biomass-based hydrogen production are twice those of coal-based hydrogen production per unit of energy. Hydrogen and electricity can also be co-produced from fossil fuels and this can reduce<del>s</del> the cost of product gas separation, and increase the plant load factor, while improving the economies of scale and reducing the CO<sub>2</sub> capture cost. FutureGen and Synfuel co-generation is a demonstration project planned in the USA and considered in the ETP model.

The supply cost of hydrogen is based on the supply volume. Distribution and refueling will add 7-9 USD to the production costs (Figure 3), these costs are for large scale systems. In a transition period, decentralized production and/or liquid hydrogen distribution may be used. Moreover, decentralized production systems cannot be combined with  $CO_2$  capture and sequestration.

#### **1.5.2.4 Gasification and Fischer-Tropsch Production of Liquid Synfuels**

Currently, gasification of carbon-containing feedstock, followed by hydrocarbon synfuel production, has received much attention, given the potential for the production of synthetic transportation fuels to reduce dependency on oil. Coal, natural gas and biomass could be used as feedstocks. Synfuel production is more energy intensive than conventional refining. Synfuels are expected to gain an increasing market share. A number of synfuels have been proposed such as methanol, DiMethyl Ether (DME), naphtha/gasoline and diesel. The energy efficiency of the production processes for these fuels ranges from 40% to 70%. So far, they produce a large volume of  $CO_2$  which could be captured and stored [5].

#### 1.6 CO<sub>2</sub> Transportation

After capturing  $CO_2$ , it must be transported to suitable storage sites.  $CO_2$  can be transported by pipelines, tank wagons or ships. In practice, because of the huge volumes involved, pipelines and ships are preferred to transport  $CO_2$  because of their cost-effective options. The cost depends on the distance and volumes involved. Generally, transportation costs are small compared to the overall capture costs. Transportation costs range approximately from 1 to 10 USD/t  $CO_2$ , provided the pipeline transports more than 1 Mt of  $CO_2$  per year and the distance is less than 500 kilometers.

#### 1.7 CO<sub>2</sub> storage

The geological storage of  $CO_2$  in the earth's upper crust is a natural phenomenon. Carbon dioxide from biological activity, volcanic activity and chemical reactions is found underground either as dissolved/precipitated carbonate minerals, or in supercritical form. Candidate geological formations for  $CO_2$  storage are depleted oil and gas reservoirs, deeply buried saline aquifers and uneconomic coal seams. Depleted oil and gas reservoirs have the advantages of well-known reservoir geology and of having infrastructures that can readily be adapted for  $CO_2$  transport and injection. On the other hand, comparatively few hydrocarbon reservoirs are currently depleted or near depletion, so that the timing of  $CO_2$  storage will depend on reservoir availability. Deep saline aquifers that could be used for long term  $CO_2$  storage are inestimable: In both cases — depleted reservoirs and saline aquifers — much of the injected gas will eventually dissolve in the formation water, while some may react with the minerals to form carbonate precipitates.

This section will focus on the following storage options:

- CO<sub>2</sub> enhanced oil recovery (EOR);
- CO<sub>2</sub> enhanced gas recovery (EGR);
- CO<sub>2</sub> enhanced coal-bed methane recovery (ECBM);
- Storage in depleted oil and gas fields;
- Storage in deep saline aquifers;

• Other storage options.

#### 1.7.1 CO<sub>2</sub> Enhanced Oil Recovery (EOR)

For three decades CO<sub>2</sub> EOR has been applied and is still considered as an established technology. However, this technology has been developed from the viewpoint of oil recovery, not from the viewpoint of CO<sub>2</sub> storage. Therefore, some adjustments may be needed for CO<sub>2</sub> storage. However, CO<sub>2</sub> EOR cannot be applied to all fields. EOR is limited to oil fields at a depth of more than 600 meters. The oil should also have a gravity of at least 23° API, equivalent to a density of, at most, 910 kg/m<sup>3</sup>. EOR is limited to oil fields where primary production (natural oil flood driven by the reservoir pressure) and secondary production methods (water flooding and pumping) have been applied. Also, the occurrence of a large gas cap limits the effectiveness of CO<sub>2</sub> flooding. Up to temperatures of 120 °C, CO<sub>2</sub> mixes with oil (a so-called miscible flood). At higher temperatures, CO<sub>2</sub> replaces the oil (a so-called immiscible flood oil). A miscible flood is more advantageous than an immiscible flood, because it results in higher oil recovery factors. Because of the physical constraints for CO<sub>2</sub> EOR, a detailed field-by-field assessment is required in order to assess its benefits properly. The ranges of  $CO_2$  storage in case of miscible EOR is from 2.4 to 3 tons of  $CO_2$  per ton of oil produced. Globally, the potential for CO<sub>2</sub> EOR is limited. That is because oil fields are not evenly distributed around the world. The regions with ample oil reserves (Middle East, FSU) are not the regions with important point sources of CO<sub>2</sub>; point sources may be far away from the oil fields. It depends on the reservoir and local supply conditions as to whether CO<sub>2</sub> flooding really is the best option from an oil recovery perspective.

#### 1.7.2 CO<sub>2</sub> Enhanced Gas Recovery

Using CO<sub>2</sub> for Enhanced Gas Recovery (EGR) is a speculative method for repressurizing depleted gas fields that can be applied to certain fields when 80-90% of the gas has been produced. Although target reservoirs for CO<sub>2</sub> sequestration are depleted in methane with pressures as low as 20-50 bars, they are not devoid of methane. Additional methane can be recovered by injecting CO<sub>2</sub> using EGR. The injected CO<sub>2</sub> to the reservoir is flowing because of pressure and gravitational effects. Regardless of phase (gaseous, liquid or supercritical) CO<sub>2</sub> is particularly denser than CH<sub>4</sub> at all relevant pressures and temperatures and will tend to flow downwards, displacing the CH<sub>4</sub> gas and repressurizing the reservoir. If CO<sub>2</sub> is injected at the bottom of a gas reservoir, it will push the gas toward the top where it can be produced. However, CO<sub>2</sub> EGR has not yet been applied anywhere in the world. Opinions are divided on whether this technology is proper for most gas fields. CO<sub>2</sub> EGR will depend on factors such as the time needed for the CO<sub>2</sub> to reach gas production wells.

If a whole reservoir was filled with  $CO_2$  up to its original pressure, about 1.8 GJ of gas could be recovered per ton of  $CO_2$  stored. The potential for  $CO_2$  use for EGR might be larger than for EOR.

#### 1.7.3 CO<sub>2</sub> Enhanced Coal-bed Methane Recovery

 $CO_2$  Enhanced Coal-Bed Methane (ECBM) is a speculative method for methane (coal gas) recovery from coal seams. ECBM increases the recovery to 90-100%, while conventional coal-bed methane recovery may achieve 40-50% recovery (close to the wells).

ECBM can only be applied to coal seams of sufficient permeability. However, because of the increasing pressure, the  $CO_2$  adsorption increases from 2 moles per mole methane at 700 meters, up to 5 moles per mole at 1,500 meters. The coal reserve should not be deeper than

2,000 meters because the increase in temperature limits the methane content of the coal and the raise pressure at greater depth causes a decrease in the coal seam permeability.

However, the following criteria must be met when screening coal reservoirs for ECBM. Only a small fraction of all coal seams meet such criteria:

- A homogeneous reservoir, laterally continuous and vertically isolated from surrounding strata;
- Minimally faulted and folded;
- At least 1-5 (mD) permeability. Most coal seams are much less permeable;
- High methane content;
- Stratigraphically concentrated coal seams are preferred over multiple thin seams;
- A possibility to use or export methane (pipeline) and CO<sub>2</sub> availability

 $CO_2$  for ECBM is the variable, and often low, permeability of the coal which is one of the major problems concerning widespread use of this technology, so coal tends to swell in contact with  $CO_2$ , which reduces permeability. Moreover, low permeability can, in some cases, be overcome by fracturing the formation.

Another general problem for coal-bed methane projects is the necessary coal dewatering, which results in lowering of the groundwater levels (for shallow reservoirs) or production of brackish/salty water (for deep reservoirs). In conclusion, CO<sub>2</sub>-ECBM technology is at an early stage of technical development and its prospects remain uncertain. Currently, new demonstration projects underway should provide valuable information on the technology and allow a decision to be made within a few years on whether this can be regarded as a safe and environmentally-acceptable mitigation option.

#### 1.7.4 Depleted Oil and Gas Fields

Depleted oil and gas reservoirs can be packed with CO<sub>2</sub>. The operation is quite simple; it just needs an injection. In addition, part of the existing infrastructure may be re-used, which can reduce the investment cost. Several injection wells might require a reservoir, depending on the field geology and the rate of injection. Most of the conventional oil and gas production resources are located in the Middle East and the former Soviet Union (FSU). However, the storage potential in depleted gas fields is much larger than in depleted oil fields. They have bigger reservoirs, and there are more of them. The storage capacity can be estimated based on the historical quantities of oil and gas produced, the actual storage potential may be reduced as the pressure cannot be brought back to the original pressure, and parts of the reservoir may be water-flooded.

#### 1.7.5 Storage in Deep Saline Aquifers

An aquifer is a layer of sedimentary rocks saturated with water and from which water can be produced through pumping, or into which fluids can be injected. Sandstone and carbonate rocks are usually aquifers. However, the pore and fracture space in sedimentary rocks are filled with water, but sandstones and carbonates have sufficient porosity to be considered for CO<sub>2</sub> storage. Some rocks do not have the porosity for such as crystalline and metamorphic rocks (granite). An aquitard is a layer of rock from which water cannot be produced, but it has enough porosity that allows the flow of water on a geological timescale like Shales. An

aquiclude is a layer of rock that has almost no porosity and does not allow the flow of water such as salt and anhydrite beds.

Open and confined aquifers have no natural barriers to water flow, and there is a natural circulation at a very low speed, while the closed aquifers have no such circulation. Therefore, they might be better suitable for CO<sub>2</sub> storage. Geological CO<sub>2</sub> sequestration in divergent basins is much safer than in convergent basins because of the tectonic stability and general lack of significant hazardous events. Sedimentary basins can be further subdivided in a number of criteria. We can indicate that not every basin is suitable for CO<sub>2</sub> storage. However, there is still considerable uncertainty regarding storage potential. The main uncertainty is to what extent the aquifer pore volume can be filled with CO<sub>2</sub>. The higher the average storage efficiency and the storage potential, the fewer the number of wells that will be required, the lower the storage costs.

The mechanisms for CO<sub>2</sub> injected in deep saline aquifers is trapped and stored by:

1) In its free phase as a plume at the top of the aquifer and in stratigraphic and structural traps

2) As bubbles that are trapped in the pore space after passing of a plume

3) Dissolved in aquifer water

 As a precipitated carbonate mineral as a result of geochemical reactions between the CO<sub>2</sub> and aquifer water and rocks.

Geochemical reaction to permanently sequester  $CO_2$  would take several thousand years to have a significant effect. Where there is no stratigraphic or structural trap, the  $CO_2$  would flow and spread over a large area below the aquifer cap rock.

More  $CO_2$  might be dissolve in the brine, if the initial  $CO_2$  saturation of the brine is lower and the required area is smaller, and the relationship could be used as part of aquifer selection criteria. The temperature profiles in underground sediments differ by location, because of variations in geothermal gradients and in surface temperatures. As a result, the state of  $CO_2$  underground will differ, as will the density at a given pressure and this affects both the storage potential per unit of surface and the relevance of leakage mechanisms.

#### **1.7.6 Other Storage Options**

There are many other storage options, such as limestone ponds, surface mineralization and oceanic storage, each of them will be discussed in this section.

The concept of limestone ponds combines capture and storage. Limestone is dissolved in water in a pond and flue gas is bubbled through this pond. The flue gas bubbles contain  $CO_2$  which reacts with the limestone. Most experts claim that it is impossible to produce bubbles that are sufficiently small ( $CO_2$  transportation into the solution is the limiting factor), and the size of the ponds would be prohibitive.

The concept of surface mineralization depends on the reaction of ground magnesium and calcium silicate rock with  $CO_2$  into carbonates. Certain types of peridotites and sepentinite would be the favored rocks, containing 40-50 weight % MgO and CaO. One tonne of  $CO_2$  would require 0.9 t of MgO, and generate 2.8 t of waste. However, conventional carbonation pathways are slow under ambient temperatures and pressures. The significant challenge being addressed by this effort is to identify an industrially and environmentally viable carbonation route that will allow mineral sequestration to be implemented with acceptable economics. In this process,  $CO_2$  is exothermically reacted with abundantly available metal oxides which produce stable carbonates. This process occurs naturally over many years and is responsible for much of the surface limestone. The reaction rate can be made faster, for example by reacting at higher temperatures and/or pressures, or by pre-treatment of the minerals,

although this method can require additional energy. Moreover, Mineralization has been considered in the Energy Technology Perspectives (ETP) model.

Another proposed form of carbon storage is oceans. Oceanic storage of  $CO_2$  is the most controversial option. There are two types of storage: dissolution in seawater and storage of  $CO_2$  hydrates or liquid  $CO_2$  at depths of more than 4,000 meters. Additionally, several concepts have been proposed for oceanic storage:

- 'Dissolution' injects CO<sub>2</sub> by ship or pipeline into the water column at depths of 1000 m or more, and the CO<sub>2</sub> subsequently dissolves.
- 'lake' deposits CO<sub>2</sub> directly onto the sea floor at depths greater than 3000 m, where
   CO<sub>2</sub> is denser than water and is expected to form a 'lake' that would delay dissolution of CO<sub>2</sub> into the environment.
- Convert the CO<sub>2</sub> to bicarbonates (using limestone).
- Store the CO<sub>2</sub> in solid clathrate hydrates already existing on the ocean floor, or growing more solid clathrate.

The environmental effects of oceanic storage are generally negative, but poorly understood. Large concentrations of  $CO_2$  kills ocean organisms, but another problem is that the storage would not be permanent if the dissolved  $CO_2$  would equilibrate with the atmosphere. Also, the acidity of the ocean water increases as part of the  $CO_2$  reacts with the water to form carbonic acid,  $H_2CO_3$ . The resulting environmental effects on benthic life forms of the bathypelagic, abyssopelagic and hadopelagic zones are poorly understood. Additionally, the bicarbonate approach could reduce the pH effects and enhance the retention of  $CO_2$  in the ocean, but this would also increase costs and other environmental effects. Using CCS with new coal and gas-fired power plants would increase electricity production costs by 2-3 US cents/kWh. In general, the process would increase the fuel requirement of a plant with CCS by about 25%, for a coal-fired plant, and about 15% for a gas-fired plant. The cost of this extra fuel, as well as storage and other system costs, are estimated to increase the costs of energy from a power plant with CCS by 30-60%, depending on specific circumstances.

Process description: flue gas is cooled and washed in the direct contact cooler then a blower introduces the flue gas to the absorber where the absorption takes place. The rich solvent is sent to the regeneration stripper and is sent back as lean amine to the absorber. The boiler consumes most of the energy, while the re-claimer shows that there is extra Opex cost due to solvent loss.

		I Market Ma
	EFG+	MEA
Total Cost	249 (M euro)	251 (M euro)
Total Opex	37.4 (M euro/ year )	41.3 (M euro/ yr)
Cost CO2 captured	62.6 (euro/ton)	66.7 (euro/ton)
Cost CO2 avoided	82.4 (euro/ton)	91.3 (euro/ ton)

Table 2: Comparison with conventional MEA process:



Fig. 1 Carbon dioxide capture after flue gas is being washed by water

Process description: The process is similar to conventional amine process where the flue gas is washed by water (refer Fig.1), then introduced to the bottom of the absorber. CO<sub>2</sub> absorption takes place and rich amine is sent to the stripper. MHI have put quite some efforts into the development of cheaper column internals and the construction of a square absorption and quench column. MHI claims that their process line-up around the reboiler bottoms will reduce energy consumption when compared to conventional amine.

#### 1.8 CO<sub>2</sub> Capture Using Hollow Fiber Membrane Contactor

Before the industrial revolution, the relatively constant concentration of  $CO_2$  in the atmosphere implied that the amounts of  $CO_2$  generated by natural processes are almost equal to that absorbed by natural processes. However, human activity, mainly burning fossil fuels, produces about 24 billion of tons of  $CO_2$  per year of which only half is being absorbed by natural processes [6]. Rangwala [7] reported that a power plant with stack gas flowrates of 500 m<sup>3</sup>/s has a typical  $CO_2$  generation rate of 400 ton/h. Henceforth, the capture of  $CO_2$  from flue gases of power plants is an effective way to prevent the threat of global warming and

approach the objectives set out by the Kyoto Agreement.  $CO_2$  can be recovered by an amine based chemical absorption process therefore forming a hybrid technology. The hollow fiber microporous membrane (HFM) is an emerging technology used for selective  $CO_2$ . The advantage of the HFM over conventional technologies is the physical size and weight reduction of the gas-liquid contacting module. Besides, the HFM offers a much larger contact area per unit volume than packed columns or tray towers, as it eliminates entrainment and flooding, and reduces foaming on operating flowrates.

The small size and light weight of these devices have been found attractive and ideal for different gas-liquid absorption applications [8]. Many investigators have focused their studies on modeling gas-liquid absorption by means of hollow fiber membrane contactors,  $CO_2$  capture by aqueous solvents [5,8,9].

The separation driving force is the concentration gradient rather than a pressure gradient. The mass transfer takes place from the gas phase through the membrane's pores and into the liquid which is still the main selectivity provider. This differentiates the membrane gas-liquid absorption from the conventional membrane processes in which the membrane itself is selective towards the species to be separated. The membrane is said to be operated under a non-wetted mode when the material is hydrophobic, i.e. the solvent does not wet the membrane and the gas mixture fills the pores, whereas the membrane is operated under a wetted mode when the material is hydrophilic, i.e. the liquid solvents spontaneously wet the membrane and fill the pores.

However, in the case of a HFM, the membrane barrier adds additional resistance to the overall mass transfer and offsets some of these advantages, especially for the wetted operating mode where the membrane pores are filled with liquid solvent, resulting in an economically non-interesting operation. For a stable operation over a prolonged period of time, the membrane's pore must remain dry, i.e. totally gas filled. Dindore [10] pointed out that the wetting of an amine based membrane depends mainly on the membrane pore size, the surface tension of the amine solution, and on the contact angle of the solution on the membrane's pore. It is understood that membrane pores are easily wetted by low surface tension solutions. The efficiency of the membrane gas absorption depends on the solubilities of the various species in the gas mixture.

Alkanolamine solutions such as MEA, DEA, DIPA (diisopropanolamine) and MDEA (*n*-methyl-diethanolamine) are very extensively used in the industrial removal of carbon dioxide and hydrogen sulfide from gas streams in natural gas, petrochemical or ammonia plants [11]. The application of satirically hindered amines such as AMP, offer higher absorption rate and capacity, better selectivity than conventional amines in the CO<sub>2</sub>removal from gas mixtures. Kim and Yang [12] have studied the removal of CO<sub>2</sub> from CO<sub>2</sub>–N<sub>2</sub>O mixture with different aqueous amine solutions, including AMP, DEA, and MDEA using PTFE membrane contactors. Recently, Wang et al. [13] modeled and simulated the performance of the CO<sub>2</sub> capture by three typical alkanolamines solutions of AMP, DEA and MDEA in a hollow fiber membrane contactor.

In this work, a numerical study was carried out to analyze the absorption of carbon dioxide in a microporous hollow fiber membrane contactor where DEA was employed as absorbents. The microscopic theoretical model based on Fick's second law includes the second order reactions of the solute in the absorbent which flows in the fiber bore of the membrane contactor [14].

24



### **Chapter 2**

#### **Modeling and Simulation**

In the subsequent analysis, the gas flow  $(CO_2)$  is assumed to circulate outside the fiber, i.e. in the shell side of the contactor, whereas the liquid absorbent (the amine solution) is flowing inside the fiber bore, i.e. the lumen of the tube. The mass transfer accompanied by the chemical reaction is taking place in the hollow fiber membrane contactor operated in a nonwetted mode, schematically shown in Fig. 2.1. The mathematical model is set based on the following assumptions:

- 1. Isothermal conditions and ideal gas behavior;
- 2. Fully developed laminar flow in the fiber side;
- 3. Chemical reaction is operated in a non-wetted mode
- 4. Steady state operated system;
- 5. Negligible axial and angular concentrations gradients;
- 6. Negligible convective transport in the angular and radial directions;
- 7. Constant gas and liquid pressures.

Using these assumptions, the concentration profiles for soluble gas and the amine solution in the liquid phase are described for cylindrical coordinates by the differential mass balances for every component as :

$$2v_{z}\left[1-\left(\frac{r}{r_{i}}\right)^{z}\right]\frac{\partial[CO2]}{\partial z} = Dco2\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial[CO_{z}]}{\partial r}\right)\right] - R_{CO_{z}}$$
(1)

$$2v_{z}\left[1-\left(\frac{r}{ri}\right)^{2}\right]\frac{\partial[R_{1}R_{2}NH]}{\partial z} = D_{R_{1}R_{2}NH}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial[R_{1}R_{2}NH]}{\partial r}\right)\right] - R_{R_{1}R_{2}NH}$$
(2)

Based on the two-step carbamate formation mechanism, the resulting reaction rate is :

$$R_{CO_2} = \left(\frac{K_Z}{1 + \frac{K_Z}{K_{Bi}[[R]_1 R_2 NH]}}\right) \left\{ [CO_2][R_1 R_2 NH] - \frac{\left(C_T - [[R_1 R_2 NH]]^2\right)}{K_{\theta q}[R_1 R_2 NH]} \right\}$$
(3)

With  $R_{R_1R_2NH} = 2R_{CO_2}$ 

The outlet gas and solvent concentration  $[CO_2]_{lo}$  and  $[R_1R_2NH]_{lo}$  are determined as "mixing cup" concentrations, given by :

(4)

(5)

$$[CO_{\mathbf{z}}]_{lo} = \frac{\int_{\mathbf{0}}^{r_{i}} 2\pi r v_{z}(r) [CO_{\mathbf{z}}]_{l} dr}{\int_{\mathbf{0}}^{r_{i}} 2\pi r v_{z}(r) dr}$$

$$[R_{1}R_{2}NH]_{lo} = \frac{\int_{0}^{r_{i}} 2\pi r v_{z}(r) [R_{1}R_{2}NH]_{l} dr}{\int_{0}^{r_{i}} 2\pi r v_{z}(r) dr}$$

$$at z = 0, [co_{\mathbf{z}}] = \mathbf{0} \quad [R_{\mathbf{1}}R_{\mathbf{z}}NH] = C_t \text{ for any } r_i \ge r \ge \mathbf{0}$$
(6)

26

$$at r = 0, \qquad \frac{\partial [CO_2]}{\partial r} = \mathbf{0}$$
(7)

$$\frac{\partial [R_1 R_2 NH]}{\partial r} = 0 \text{ for any } l \ge z \ge 0$$

$$at r = ri, D_{CO_2} \frac{\partial [CO_2]}{\partial r} = K_{ext} \{ [CO_2]^{int} - [CO_2]^{r=ri} \}$$
(9)

(8)

(10)

$$\frac{\partial [R_1 R_2 NH]}{\partial r} = 0 \text{ for any } l \ge z \ge 0$$

$$\xi = \frac{r}{ri}, \qquad \zeta \frac{z}{l}, \qquad \Phi_{Al} = \frac{[CO_2]}{[CO_2]^{int}} = \frac{[CO_2]_l}{m[CO_2]_g}, \\ \Phi_{Bl} = \frac{[R1R2NH]_l}{C_T}$$
(11)

$$\frac{\partial \Phi_{AI}}{\partial \varsigma} = \left(\frac{1}{1-\xi^2}\right) \left\{ \frac{2}{Gr_A} \left[ \frac{\partial^2 \Phi_{AI}}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \Phi_{AI}}{\partial \xi} \right] - \frac{1}{2} \left( \frac{\beta_1 \Phi_{BI}}{\beta_3 + \Phi_{BI}} \right) \left[ \Phi_{AI} \Phi_{BI} - \frac{(1-\Phi_{BI})^2}{\beta_4 \Phi_{BI}} \right] \right\}$$
(12)

$$\frac{\partial \Phi_{BI}}{\partial \varsigma} = \left(\frac{1}{1-\xi^2}\right) \left\{ \frac{2}{Gr_B} \left[ \frac{\partial^2 \Phi_{BI}}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \Phi_{BI}}{\partial \xi} \right] - \left( \frac{\beta_2 \Phi_{BI}}{\beta_3 + \Phi_{BI}} \right) \left[ \Phi_{AI} \Phi_{BI} \frac{(1-\Phi_{BI})^2}{\beta_4 \Phi_{BI}} \right] \right\}$$
(13)

$$at\varsigma = 0, \Phi_{AI} = 0$$
  

$$\Phi_{BI} = 1 \quad for \; any \; 1 \ge \xi \ge 0$$
  

$$at\varsigma = 0 \quad \left| \frac{\partial \Phi_{AI}}{\partial \xi} \right|_{\xi=0} = 0$$
(14)

$$\begin{aligned} \left| \frac{\partial \Phi_{BI}}{\partial \xi} \right|_{\xi=0} &= 0 \ for \ any \ 1 \ge \varsigma \ge 0 \end{aligned} \tag{15}$$

$$at \ \xi = 1 \quad \left. \frac{\partial \Phi_{AI}}{\partial \xi} \right|_{\xi=1} = \frac{Sh_{\theta xt}}{2} \left[ |1 - \Phi_{AI}|_{\xi=1} \right] \tag{16}$$

$$\left| \frac{\partial \Phi_{BI}}{\partial \xi} \right|_{\xi=1} &= 0 \ for \ any \ 1 \ge \varsigma \ge 0 \tag{17}$$

$$Gr_A = \frac{\overline{v}_z d_i^2}{l D_{CO2}}, \qquad Gr_B = \frac{\overline{v}_z d_i^2}{l D_{R_1 R_2 N H}}$$
(18)

$$\beta_{1=} \frac{lK_Z C_t}{\overline{v}_Z} \beta_2 = \frac{lK_Z m[CO_2]_g}{\overline{v}_Z} \quad \beta_{1=} \frac{k-z}{k_{Bi} C_T} \quad \beta_{2=} \frac{k-z}{k_{Bi} C_$$

$$\frac{k_{Ag}d_{e}}{D_{Ag}} = 1.8 \left(\frac{d_{e}}{l}\right)^{0.92} \left(\frac{d_{e}\overline{v}_{z}}{v_{Ag}}\right)^{0.92} \left(\frac{v_{Ag}}{D_{Ag}}\right)^{0.92}$$
(20)

$$\Phi_{Alo} = 4 \int_0^1 \xi (1 - \xi^2) \Phi_{Al} d\xi$$
(21)

$$\Phi_{Blo}=4\int_0^1\xi(1-\xi^2)\Phi_{Bl}d\xi$$

5

$$\eta co_{\mathbf{z}} = \frac{[CO_{\mathbf{z}}]_{li} - [CO_{\mathbf{z}}]_{lo}}{[CO_{\mathbf{z}}]_{li}} = \mathbf{1} - \Phi_{\mathbf{Alo}}$$

(22)

. . .

(23)

28



#### **Chapter 3**

#### **Results and Discussion**

In the following section, the effect of operating parameters on conventional industrial absorber and polymeric hollow fiber membrane were investigated.

#### 3.1 Conventional Industrial Absorber

In order to remove  $CO_2$  from the feed stream, two main vessels are needed: an absorber and a stripper. Inside the absorber, chemical reactions will occur in which the  $CO_2$  is chemically absorbed into the solvent and this compound, along with water, will flow out the bottom of the absorber. That stream will then go through a flash chamber to lower the temperature and pressure of the liquid (and to separate out some  $CO_2$ ) before proceeding onto the stripper where the  $CO_2$  will separate out from the solvent.

An industrial absorber was studied on a normal operating unit in the Ammonia Plant complex. Unit is designed to recover 450 tons/day CO<sub>2</sub>. The process employs structured packing in the flue gas water cooler and CO<sub>2</sub> absorber. A specialized proprietary demister has also been installed after washing section. The LP steam and cooling water are the major utilities required. The flue gas is extracted from the discharge of ID fan of primary reformer. The design data for the unit is as follows:

Flue gas feed	:	132500 NM <sup>3</sup> /hr
Flue gas temp.	:	180 <sup>0</sup> C
Flue gas temp. inlet absorber	:	40 <sup>0</sup> C

29

Flue gas press.	:	615 mm WC
Lean solution flow rate	:	195 ton/hr
CO <sub>2</sub> flow rate	1. set	18.8 ton/hr

The data sets were collected for different gas flow rates and at varying inlet gas pressures. In an industrial operating unit, it is not practical to isolate the parameters completely. In spite of varying only one parameter, other factors will always influence the changes.

#### Effect of pressure

As is expected from the principles of absorption, the increase in pressure improves the recovery of  $CO_2$  from the incoming gas (Table 3, Fig.2). Initially the increase in recovery rate is somewhat prominent, when the driving force is more. But it rises slowly when the pressure increases beyond 550 mm water column. This is quite logical as the equilibrium is reached with respect to the partial pressure of CO2 in the gas phase.

#	Press, mm WC	Product CO2 flow, tons/hr
set 1	265	11.4
set 2	287.7	11.8
set 3	436	14.2
set 4	456	17.17
set 5	468.4	17.2
set 6	454	17.23
set 7	453	17.58
set 8	457	17.68
set 9	615	18.80

Table 3: CO<sub>2</sub> recovery vs. pressure



Fig. 2 Pressure versus CO<sub>2</sub> recovered

#### Effect of temperature

The increase in temperature initially increases the recovery of  $CO_2$  from incoming gas due to an improvement in the reaction rate (Table 4, Fig.3). However, beyond a certain point, the recovery of  $CO_2$  flattens out. The reason can be explained thus – A rise in temperature increases the reaction rates, but as the temperatures increase – the system moves towards a zone which works against the principles of absorption, i.e. absorption is favored by low temperatures.

#	Temp., °C	Product CO <sub>2</sub> flow, tons/hr
Set1	55.2	11.4
set 2	54.7	11.8
set 3	56.8	14.2
set 4	59	17.17
set 5	61.5	17.2
set 6	61	17.23
set 7	61.3	17.58

 Table 4: CO2 recovery vs. temperature

#### Temperature vs. CO2 recovered



Fig. 3. Temperature versus product carbon dioxide flow rate

#### Effect of Flue gas rates

As could be expected, the increase in incoming flue gas rates improves the recovery of  $CO_2$  from the incoming gas (Table 5, Fig.4). The slope of the graph improves at the higher input rates as increases in the gas flow rates changes the partial pressure profile of the  $CO_2$  component.

	Gas flow rate, NM <sup>3</sup> /HR	Product CO2 flow, tons/hr
set 1	82007	11.4
set 2	92561	11.8
set 3	108702	14.2
set 4	110983	17.17
set 5	107187	17.2
set 6	110685	17.68

 Table 5: CO2 recovery vs. gas flow rate

#### Gas Flow Rate vs. CO2 recovered





#### Effect of Solvent flow rate

Again, as could be expected, the increase in the solution flow rate improves the recovery of  $CO_2$  from the incoming gas (Table 6, Fig.5). The rise in  $CO_2$  recovery initially is quite enhanced, but beyond a certain point, becomes a normal rise slowing down to an asymptotic curve. The reason for this can be explained thus – Initially,  $CO_2$  recovery increases with the rise in solution flow rates but only to the extent as per the margins available on the  $CO_2$  partial pressures. In reality, industrial absorbers are not designed for 100% efficiency, due to the optimum design and economic considerations. Hence, we can extract only as much  $CO_2$ 

where the recovery is possible by the partial pressure limit (fraction component in the incoming gas).

#	Solvent flow rate, tons/hr	Product CO2 flow, tons/hr
set 1	223.4	11.4
set 2	225.4	11.8
set 3	233	14.2
set 4	244	17.17
set 5	243	17.2
set 6	240	17.23
set 7	245	17.58
set 8	242	17.68

Table 6: CO2 recovery vs. solvent flow rate





Fig. 5 Solvent flow rate versus CO<sub>2</sub> recovered

#### 3.2 Polymeric Hollow Fiber Membrane

The hollow fiber module used in this study is similar to that employed by Boucif, et al. [15].

The geometrical properties are shown in Table below :

 Table 7
 Specifications of the HF contactors used in this study.

Characteristics	Values
Fibers material	Polypropylene
Fiber inner diameter (µm)	330
Fiber outer diameter (µm)	360
Fiber thickness (µm)	15
Average pore size <u>r</u> <sub>p</sub> (μm)	0.06
Porosity E	0.6
Number of fibers	1930
Active module length (mm)	200
Inner contact area (m <sup>2</sup> )	0.40
Outer contact area (m <sup>2</sup> )	0.4363

Typical concentration profiles for the carbon dioxide and DEA species are shown in Fig. 6. The cartridge module length has a considerable effect on both outlet carbon dioxide and amine concentrations. The longer the module, the higher is the residence time, thus the greater the absorption efficiency. For longer modules, the residence time is sufficiently high and chemical equilibrium can be reached. For instance, long membrane modules allow higher carbon dioxide removing, and both gas and amine outlet concentrations reach asymptotic values as the chemical equilibrium is obtained. Figure 7 is a 3D diagram that shows the concentration of Carbon Dioxide as a function of module radius and length. The concentration of carbon dioxide increases through the length of the module, by contrast, the  $CO_2$  concentration decreases with the increase in the radius, since  $CO_2$  is flowing in the shell side in a counter current profile mode. Figure 11 is 3D diagram that shows the concentration of amine concentration as a function of module radius and length. The amine concentration is almost pure at the module inlet. The concentration of amine decreases with module length, due to continuous absorption of  $CO_2$ , by contrast, the amine concentration increases with the increase in the radius, since amine is flowing in the side.



Fig. 6 Dimensionless CO<sub>2</sub> and DEA concentration as a function the fiber length



Fig. 7 Carbon dioxide concentration profile as a function of membrane radius and length



Fig. 8 DEA concentration profile as a function of radius and length

Fig. 9 depicts the effects of liquid velocity on the dimensionless amine concentration. The figure shows that for very low liquid velocities, (< 0.001 m/s equivalent to10 cc/min) the amine concentration is almost close to zero, whereas for very high liquid velocities (> 0.1 m/s equivalent to 1000 cc/min) the decrease in the amine concentration varied slightly. However, in between that calculated range, the DEA solution presents a higher trend for the carbon dioxide absorption. The interfacial carbon dioxide depletion extent in the liquid solutions increases with an increase in the liquid velocity. It is advised from these findings that the efficiency of carbon dioxide absorption in hollow fiber membrane contactors is optimized when lower liquid velocities are employed.

Fig. 10 depicts the liquid velocity effects on the fiber outlet interfacial carbon dioxide depletion extent in the liquid phase for DEA amine. The figure shows that for very low liquid velocities, (0.001 m/s equivalent to 10 cc/min) the carbon dioxide is almost completely absorbed, whereas for very high liquid velocities (> 0.1 m/s equivalent to 1000 cc/min) the absorption remains basically unchanged. However, in between that calculated range, the DEA solution presents a higher trend for the carbon dioxide absorption capacity.

The interfacial carbon dioxide depletion extent in the liquid solutions increases with an increase in the liquid velocity. It is advised from these findings that the efficiency of carbon dioxide absorption in hollow fiber membrane contactors is optimized when lower liquid velocities are employed.



Fig. 9 Effect of liquid velocity in the fiber lumen on Amine concentration



Fig. 10 Effect of liquid velocity in the fiber lumen on CO<sub>2</sub> concentration

In Figure 11, the outlet carbon dioxide depletion extent is plotted as a function of the total inlet amine concentration. The figure shows that the initial concentration of the DEA solution has a high influence on the gaseous outlet concentration. The carbon dioxide absorption seems to be substantially enhanced when the initial concentration of the absorbent solution is increased until saturation is reached beyond a value greater that 10<sup>4</sup> mol/m<sup>3</sup>. Nevertheless, it must be known that a higher absorbent concentration could have harmful side-effects and cause irreversible damages to the hollow fiber membrane material, as well as corrosion in the other metallic components. The carbon dioxide absorption being essentially limited by the reaction kinetics, the choice of the optimal inlet amine concentration is, therefore, dictated by a compromise among these operating requirements.



Fig. 11 Effect of initial total amine concentration on outlet CO<sub>2</sub> depletion extent

#### CONCLUSION

A mathematical model for the simulation of the hollow fiber membrane gas-liquid absorption was developed. The coupled non-linear partial differential and algebraic equations derived in the mathematical model explicitly account for the rates of mass transfer through the membrane, diffusion and chemical reaction in the liquid phase. The equations were solved using gPROMs software package. It was found that the liquid velocity and initial absorbent concentrations, as well as the fiber inner diameter and length, have a tremendous effect on the carbon dioxide removal performance.

#### REFERENCES

[1] Strelzoff, Samuel, iSection 3: Carbon Dioxide Absorption Technology and Manufacture of Ammonia, Robert E. Krieger Publishing Company, Inc.: 1988, pp. 193-248.

[2] IEA World Energy Outlook scenario 2002.

[3] Twigg, Martyn V., Catalyst Handbook: second edition, Manson Publishing Ltd: 1996, pp. 80, 340-343, 404-409.

[4] Encyclopedia of Industrial Chemistry. Vol A.5, pp. 172-175

[5] Morrissey, W.A., Justus, J.R., 2002. Global Climate Change. Cambridge Scientific Abstracts.

[6] Rangwala, 1996 H.A. Rangwala, Absorption of carbon dioxide into aqueous solutions using hollow fiber membrane contactors, *Journal of Membrane Science* 112 (1996), pp. 229–240.

[7] S.R. Wickramasinghe, M.J. Semmens and E.L. Cussler, Mass-transfer in various hollow fiber geometries, *Journal of Membrane Sciences* 69 (1992), pp. 235–250.

[8] H. Kreulen, C.A. Smolders, G.F. Versteeg and W.P.M. van Swaaij, Microporous hollow fiber membrane modules as gas-liquid contactors Part 2. Mass transfer with chemical reaction, *Journal of Membrane Science* 78 (1993), pp. 217–238.

[9] M. Mavroudi, S.P. Kaldis and G.P. Sakellaropoulos, A study of mass transfer resistance in membrane gas-liquid contacting processes, *Journal of Membrane Science* 272 (2006), pp. 103–115.

[10] V.Y. Dindore, D.W.F. Brilman, F.H. Geuzebroek and G.F. Versteeg, Membrane solvent selection for CO<sub>2</sub> removal using membrane gas-liquid contactors, Journal of Separation and purification technology **ISSN** 1383-5866 2004, vol. 40, no.2, pp. 133-145.

[11] A .L. Kohl and F.C. Riesenfeld, Gas Purification (fourth ed), Gulf Publishing, Houston, TX, USA (1985).

[12] Y.S. Kim and S.M. Yang, Absorption of carbon dioxide through hollow fiber membranes using different aqueous absorbents, *Separation and Purification Technology* 21 (2000), pp. 101–109

[13] R. Wang, D.F. Li and D.T. Liang, Modeling of CO<sub>2</sub> capture by three typical amine solutions in hollow fiber membrane contactors, *Chemical Engineering and Processing* 43 (2004), pp. 849–856.

[14] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, The Netherlands (1996).

[15] N. Boucif, E. Favre, D. Roizard and M. Belloul, Hollow fiber membrane contactor for hydrogen sulfide odor control, *A.I.Ch.E. Journal* 54 (2008), pp. 122–131.

يعتقد بأن ظاهرة الإحتباس الحراري العالمي وتغيير المناخ سببه الرئيسي إنبعائات الغازات النفيئة. ويعتبر ثاني أكسيد الكربون العامل الرئيسي في تغير المناخ العالمي الذي يؤدي مباشرة إلى مشاكل بيئية خطيرة. الن نصف مصادر إنبعاث ثاني أكسيد الكربون من نشاط الإنسان تأتي نتيجة لإحتراق الوقود الأحفوري في من الغازات الخارجة من المداخن بإستخدام أداة إمتصاص تقليدية و أغشية نسيجية بوليمرية نفاذة مجوفة. ويتم مقارنة بيانات أداة الإمتصاص الصناعية بالبيانات الظاهرة بإستخدام الأغشية النسيجية النفاذة المجوفة عن طريق حزمة برامج النظام العام لتمثيل العمليات. وفي هذا التحليل، مع تدفق محلول الإمتصاص في عن طريق حزمة برامج النظام العام لتمثيل العمليات. وفي هذا التحليل، مع تدفق محلول الإمتصاص في عن طريق حزمة برامج النظام العام لتمثيل العمليات. وفي هذا التحليل، مع تدفق محلول الإمتصاص في الجانب الداخلي من التجويف النسيجي والغاز النقي في نموذج يعمل بطريقة الفروق الخلفية المحدودة. المعادلات القاضلية الجزئية غير الخطبة المزدوجة المستمدة من خلل طريقة الفروق الخلفية المحدودة. من حيث سرعة النائي والتركيز الأولي للأمينات والمعامل الخارجي لنقل العالية المحدودة. ويستعمل ثنائي ثانو لامين كأداة إمتصاص. يتم تقليد تركيز ثاني أكسيد الكربون الممتص المخرج ودراسته من حيث سرعة السائل والتركيز الأولي للأمينات والمعامل الخارجي لنقل الكماتي المندروبة المعادين والمربة الورق الخلفية المحدودة. والم حول الألياف على تركيز الغاز النقي في نموذج يعمل بطريقة الفروق الخلفية المحدودة. قطر وطول الألياف على تركيز الغاز الخارج كنتيجة لمر عة مرور السائل. وقد تبين أن سرع عة السائل والتركيزات الأولية للإمتصاص وكذلك القطر الداخلي وظول الألياف لما أكبر الأثر على عملية إز الة ثاني

ملخص

### شكر وتقدير

أود أن أعرب عن عميق شكري وإمتناني للدكتور نايف جاسم الذي أشرف على أطروحتي وزودني بملاحظات و اقتراحات القيمة، كما أود أن أشكر منسق برنامج الماجستير الأستاذ الدكتور عبد الرزاق زكري على لطف و وتشجيع ومساعدت المستمرة خلال فترة دراستي، وأتوجه بجزيل الشكر إلى الأستاذ كمال مصطفى والأستاذ طارق فارس على موافقتهما للإنضمام إلى لجنة مناقشة رسالتي، كما أود أن أشكر فريق مهندسي فرتيل على تزويدي بالبيانات الفنية والتعليقات القيمة.





جامعة الإمارات العربية المتحدة عمادة الدراسات العليا

برنامج ماجستير علوم وهندسة البترول

إستخلاص غاز ثاني أكسيد الكربون من عوادم الإحتراق

محمد راشد الراشد

اعداد

قدمت الأطروحة إلى جامعة الإمارات العربية المتحدة ضمن متطلبات الحصول على درجة الماجستيسر في علوم وهندسة البترول

Shrie en

Digitally signed by Shrieen DN: cn=Shrieen, o=UAE University, ou=UAEU Libraries Deanship, email=shrieen@uaeu.ac.ae, c=US Date: 2016.09.08 08:36:09 +02'00'

2009