2009

Carbon dioxide capture from Flue gases

Mohamed Rashid Al Rashid

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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
Thesis Title
Carbon Dioxide Capture from Flue Gases

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<th>No.</th>
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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)

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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 CO₂ 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.
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Nomenclature

$A_T$ total surface area of gas liquid contact, $m^2$

$A_{i,j}$ matrix coefficients of the weight first derivative

$B_{i,j}$ matrix coefficients of the weight second derivative

$C_T$ total amine concentration, $mol/m^3$

$D_i$ inner fiber diameter, $m$

$D_{lm}$ logarithmic mean average diameter

$d_o$ outer fiber diameter, $m$

$D_{Ag}$ diffusion coefficient of specie CO$_2$ in air, $m^2/s$

$D_{AK}$ continuum Knudsen diffusion coefficient of specie CO$_2$, $m^2/s$

$E$ dimensionless enhancement factor

$Gr$ dimensionless Graetz number

$H$ dimensionless Henry's law constant, dimensionless

$k_{Ag}$ gas film mass transfer coefficient of specie A, $m/s$

$k_{Al}$ liquid film mass transfer coefficient of specie A, $m/s$

$k_{Am}$ membrane mass transfer coefficient of specie A, $m/s$

$k_{Bi}$ forward second order reaction rate constant

$k_{ov}$ overall reaction rate constant, $m/s$

$k_{Z}$ forward second order reaction rate constant

$k_{Z}$ reverse second order reaction rate constant

$\lambda$ equilibrium constant

$K_{ext}$ external mass transfer coefficient, $m/s$

$K_{ov}$ 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

$r_i$ inner fiber radius
Greek letters

ς    dimensionless axial coordinate  
δ    membrane thickness  
η    extent of gas removal  
ξ    dimensionless radial coordinate  
ξi   collocation point  
Φii  dimensionless concentration of specie i in the liquid phase  
Φii1 dimensionless inlet concentration of specie i in the liquid phase  
Φiio dimensionless outlet concentration of specie i in the liquid phase  
τ    membrane's pore tortuosity
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 CO₂ 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 CO₂ will be in the atmosphere by 2050, if CCS is not used. In addition to being stored underground, CO₂ 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 (CO₂) from large point sources such as fossil fuel power plants. Currently, CCS is gaining attention as an option for reducing CO₂ emissions, and covers a broad range of technologies that are being developed to allow carbon dioxide (CO₂) 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 CO₂ 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 CO₂ Emission

The world’s dependence on fossil fuels for the satisfaction of primary energy needs cause increasing atmospheric emissions of CO₂ 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 CO₂ emissions.

Moreover, as fossil fuel based heat and power production counted as sources of CO₂ emission, there are also other large stationary sources of CO₂ 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 CO₂ in the environment will also increase and consequently, the environment will continue to suffer serious problems because of the increase in CO₂ emissions. The concentration of CO₂ 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 CO₂ 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 CO₂. The concentration of CO₂ in the air exceeds 1,000 ppm CO₂ [2].

In general, the global CO₂ emissions increased by 70% between 1971 and 2002. Since 1990 CO₂ 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, CO₂ 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 CO₂ 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 CO₂ emission through the past three decades was as follows: burning of coal caused an increase in global CO₂ emissions by 40%, oil is responsible for 31% and gas 29% [3].

1.3 CO₂ Capture and Storage CCS Processes

CO₂ Capture and Storage (CCS) include three distinct processes, first; capturing CO₂ from the gas streams emitted during electricity production, industrial processes or fuel processing;
second, transporting the captured CO₂ by pipeline or in tankers; and third, storing CO₂ 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**

<table>
<thead>
<tr>
<th>CCS projects</th>
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<td>CO₂ capture demonstration projects</td>
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<td>CO₂ capture R&amp;D projects</td>
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<td>Geologic storage R&amp;D projects</td>
<td>74</td>
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<td>Ocean storage R&amp;D projects</td>
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There are many small-scale pilot plants based on new capture technologies are in operation around the world.

### 1.4 Capturing CO₂

By using the new, existing and the emerging technologies, CO₂ can be captured either before or after combustion. In conventional processes, CO₂ is captured from the flue gases produced during combustion (post-combustion capture) and it is also possible to convert the hydrocarbon fuel into CO₂ and hydrogen by removing the CO₂ from the fuel gas and combust the hydrogen (pre-combustion capture).

The pre-combustion depends on the physical absorption of CO₂ 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\textsubscript{2} 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\textsubscript{2} 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\textsubscript{2} Capture Sources

CO\textsubscript{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\textsubscript{2} emissions and capturing CO\textsubscript{2} from coal, natural gas, oil and biomass-fired power plants. The second source is industrial processes from which CO\textsubscript{2} can be captured from the production processes of iron, cement, chemicals and pulp, activities which generate a combined 23% of world CO\textsubscript{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 CO₂ 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 CO₂ Capture in the Manufacturing Industry

CO₂ capture could be applied in many production processes in the manufacturing industry. Industrial sources of relatively pure CO₂ 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 CO₂ concentrations but with large quantities of CO₂, but because of the low concentrations of CO₂, they would require either costly and energy-intensive CO₂ chemical absorption processes, or process re-design to increase CO₂ concentrations, such as those based on the use of oxygen in combination with post-combustion CO₂ removal or hydrogen production in combination with pre-combustion CO₂ 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, CO₂ was separated from the hydrogen before the ammonia production step, while in new plants, hydrogen, rather than CO₂, is separated from the syngas. The remaining gas containing CO₂, CO, unconverted methane, etc., is used as a fuel in the reformer furnace. In this case, there is no pure CO₂ stream, if there was a need to produce pure CO₂ it would be
switched back to the old plant design. The separated CO₂ is used for the production of urea (CH₄N₂O), a popular type of nitrogen fertilizer and 0.88 tons of CO₂ are needed for each tone of urea produced. The Energy use for ammonia production amounts to 25-40 GJ/t, resulting 1.5 tons CO₂ emission per ton of ammonia.

1.5.1.2 Iron and Steel Production

The amounts of CO₂ are captured in the iron and steel industry in the production of Direct Reduced Iron (DRI) and the CO₂ is released into the atmosphere. Global DRI production amounted to 38 Mt in 2001, which caused about 20-30 Mt CO₂ 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 CO₂. As secondary steel production grows, the iron production is planned to be around 350-400 Mt in 2030. The CO₂ emissions from blast furnaces amounts to 1-1.5 t/t iron and this CO₂ can be removed by re-designing the blast furnace for oxygen use and, subsequently, removing CO₂ using physical absorbents but this strategy has received limited attention. Additionally, if CO₂ 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 CO₂ per year, equal to 0.6-1.0 t CO₂ per tonne of Portland cement, depending on fuel and energy efficiency. As the cement production is increasing, CO₂ emissions from this source category are rising. In the off-gases, CO₂
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):

\[ CaCO_3 \rightarrow CaO + CO_2 \]

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$_2$ 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 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 CO₂ capture could be applied to these production processes. There are four categories of CO₂ capture from fuel supply:

- CO₂ capture in natural gas processing;
- Refinery CO₂ capture;
- Hydrogen production processes;
- Gasification and Fischer-Tropsch production of synfuels.

1.5.2.1 Natural Gas Processing

The CO₂ 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 CO₂ content is 1-2%. The magnitude of CO₂ that is released when the gas is combusted is larger than the CO₂ from gas processing, and this will limit the worldwide potential for CO₂ capture in natural gas processing to less than 100 Mt CO₂ 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. CO₂ should be captured before the gas can be sold, as storage sites are often nearby. Moreover, CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture technology. A study for a UK refinery and petrochemical complex suggests that collecting 2 Mt of CO₂ 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 CO₂.

To reduce the concentration of NOx and SO₂, 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 CO₂ 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 CO₂ 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 CO₂-free energy carrier. When hydrogen is produced from carbon-containing energy carriers, CO₂ 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 CO₂ capture, followed by hydrogen production from other CO₂-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 CO₂ 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 the cost of product gas separation, and increase the plant load factor, while improving the
economies of scale and reducing the CO₂ 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 CO₂ 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 CO₂ which could be captured and stored [5].

1.6 CO₂ Transportation

After capturing CO₂, it must be transported to suitable storage sites. CO₂ can be transported by pipelines, tank wagons or ships. In practice, because of the huge volumes involved, pipelines and ships are preferred to transport CO₂ 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 CO₂, provided the pipeline transports more than 1 Mt of CO₂ per year and the distance is less than 500 kilometers.

1.7 CO₂ storage

The geological storage of CO₂ 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 CO₂ 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 CO₂ transport and injection. On the other hand, comparatively few hydrocarbon reservoirs are currently depleted or near depletion, so that the timing of CO₂ storage will depend on reservoir availability. Deep saline aquifers that could be used for long term CO₂ 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:

- CO₂ enhanced oil recovery (EOR);
- CO₂ enhanced gas recovery (EGR);
- CO₂ enhanced coal-bed methane recovery (ECBM);
- Storage in depleted oil and gas fields;
- Storage in deep saline aquifers;
Other storage options.

1.7.1 CO₂ Enhanced Oil Recovery (EOR)

For three decades CO₂ 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 CO₂ storage. Therefore, some adjustments may be needed for CO₂ storage. However, CO₂ 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/m³. 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 CO₂ flooding. Up to temperatures of 120 °C, CO₂ mixes with oil (a so-called miscible flood). At higher temperatures, CO₂ 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 CO₂ EOR, a detailed field-by-field assessment is required in order to assess its benefits properly. The ranges of CO₂ storage in case of miscible EOR is from 2.4 to 3 tons of CO₂ per ton of oil produced. Globally, the potential for CO₂ 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 CO₂; point sources may be far away from the oil fields. It depends on the reservoir and local supply conditions as to whether CO₂ flooding really is the best option from an oil recovery perspective.
1.7.2 CO₂ Enhanced Gas Recovery

Using CO₂ 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 CO₂ 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 CO₂ using EGR. The injected CO₂ to the reservoir is flowing because of pressure and gravitational effects. Regardless of phase (gaseous, liquid or supercritical) CO₂ is particularly denser than CH₄ at all relevant pressures and temperatures and will tend to flow downwards, displacing the CH₄ gas and repressurizing the reservoir. If CO₂ is injected at the bottom of a gas reservoir, it will push the gas toward the top where it can be produced. However, CO₂ EGR has not yet been applied anywhere in the world. Opinions are divided on whether this technology is proper for most gas fields. CO₂ EGR will depend on factors such as the time needed for the CO₂ to reach gas production wells.

If a whole reservoir was filled with CO₂ up to its original pressure, about 1.8 GJ of gas could be recovered per ton of CO₂ stored. The potential for CO₂ use for EGR might be larger than for EOR.

1.7.3 CO₂ Enhanced Coal-bed Methane Recovery

CO₂ 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 CO₂ 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 15
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 CO₂ availability

CO₂ 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 CO₂, 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, CO₂-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 CO₂. 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 CO₂ 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 CO₂ storage. Geological CO₂ 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 CO₂ 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 CO₂. 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 CO₂ 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
4) As a precipitated carbonate mineral as a result of geochemical reactions between the CO₂ and aquifer water and rocks.

Geochemical reaction to permanently sequester CO₂ would take several thousand years to have a significant effect. Where there is no stratigraphic or structural trap, the CO₂ would flow and spread over a large area below the aquifer cap rock.

More CO₂ might be dissolve in the brine, if the initial CO₂ 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 CO₂ 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 CO₂ which reacts with the limestone. Most experts claim that it is impossible to produce bubbles that are sufficiently small (CO₂ 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 CO₂ into carbonates. Certain types of peridotites and seepentinite would be the favored rocks, containing 40-50 weight % MgO and CaO. One tonne of CO₂ 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, CO₂ 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\textsubscript{2} is the most controversial option. There are two types of storage: dissolution in seawater and storage of CO\textsubscript{2} hydrates or liquid CO\textsubscript{2} at depths of more than 4,000 meters. Additionally, several concepts have been proposed for oceanic storage:

- 'Dissolution' injects CO\textsubscript{2} by ship or pipeline into the water column at depths of 1000 m or more, and the CO\textsubscript{2} subsequently dissolves.
- 'lake' deposits CO\textsubscript{2} directly onto the sea floor at depths greater than 3000 m, where CO\textsubscript{2} is denser than water and is expected to form a 'lake' that would delay dissolution of CO\textsubscript{2} into the environment.
- Convert the CO\textsubscript{2} to bicarbonates (using limestone).
- Store the CO\textsubscript{2} 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\textsubscript{2} kills ocean organisms, but another problem is that the storage would not be permanent if the dissolved CO\textsubscript{2} would equilibrate with the atmosphere. Also, the acidity of the ocean water increases as part of the CO\textsubscript{2} reacts with the water to form carbonic acid, H\textsubscript{2}CO\textsubscript{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\textsubscript{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 reclaimer shows that there is extra Opex cost due to solvent loss.

Table 2: Comparison with conventional MEA process:

<table>
<thead>
<tr>
<th></th>
<th>EFG+</th>
<th>MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Cost</td>
<td>249 (M euro)</td>
<td>251 (M euro)</td>
</tr>
<tr>
<td>Total Opex</td>
<td>37.4 (M euro/ year)</td>
<td>41.3 (M euro/ yr)</td>
</tr>
<tr>
<td>Cost CO₂ captured</td>
<td>62.6 (euro/ton)</td>
<td>66.7 (euro/ton)</td>
</tr>
<tr>
<td>Cost CO₂ avoided</td>
<td>82.4 (euro/ton)</td>
<td>91.3 (euro/ton)</td>
</tr>
</tbody>
</table>
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. CO₂ 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 CO₂ Capture Using Hollow Fiber Membrane Contactor

Before the industrial revolution, the relatively constant concentration of CO₂ in the atmosphere implied that the amounts of CO₂ 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 CO₂ 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 m³/s has a typical CO₂ generation rate of 400 ton/h. Henceforth, the capture of CO₂ 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. CO₂ 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 CO₂. 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, CO₂ 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 CO₂ removal from gas mixtures. Kim and Yang [12] have studied the removal of CO₂ from CO₂–N₂O 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 CO₂ 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].
Chapter 2
Modeling and Simulation

In the subsequent analysis, the gas flow (CO₂) 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 non-wetted 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:
\[ 2v_z \left[ 1 - \left( \frac{r}{r_f} \right)^3 \right] \frac{\partial [CO_2]}{\partial z} = D_{CO_2} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial [CO_2]}{\partial r} \right) \right] - R_{CO_2} \]  \hspace{1cm} (1)

\[ 2v_z \left[ 1 - \left( \frac{r}{r_f} \right)^3 \right] \frac{\partial [R_1R_2NH]}{\partial z} = D_{R_1R_2NH} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial [R_1R_2NH]}{\partial r} \right) \right] - R_{R_1R_2NH} \]  \hspace{1cm} (2)

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

\[
R_{CO_2} = \left( \frac{K_z}{1 + \frac{K_z}{K_{B1}[R_1R_2NH]}} \right) \left\{ [CO_2][R_1R_2NH] - \left( \frac{C_T - [R_1R_2NH]^2}{K_{eq}[R_1R_2NH]} \right) \right\} \hspace{1cm} (3)
\]

With \( R_{R_1R_2NH} = 2R_{CO_2} \)

The outlet gas and solvent concentration [CO₂]₀ and [R₁R₂NH]₀ are determined as "mixing cup" concentrations, given by:

\[
[CO_2]_0 = \frac{\int_0^r 2\pi r v_z(r)[CO_2]_0 \, dr}{\int_0^r 2\pi r v_z(r) \, dr} \hspace{1cm} (4)
\]

\[
[R_1R_2NH]_0 = \frac{\int_0^r 2\pi r v_z(r)[R_1R_2NH]_0 \, dr}{\int_0^r 2\pi r v_z(r) \, dr} \hspace{1cm} (5)
\]

at \( z = 0, [CO_2] = 0 \) \( [R_1R_2NH] = C_t \) for any \( r_i \geq r \geq 0 \)  \hspace{1cm} (6)

26
at \( r = 0 \), \( \frac{\partial [CO_2]}{\partial r} = 0 \) \hspace{1cm} (7)

\[
\frac{\partial [R_1R_2NH]}{\partial r} = 0 \text{ for any } l \geq z \geq 0
\] \hspace{1cm} (8)

\[
\frac{\partial [R_1R_2NH]}{\partial r} = 0 \text{ for any } l \geq z \geq 0
\] \hspace{1cm} (10)

\[
\xi = \frac{r}{r_i}, \quad \frac{z}{l}, \quad \Phi_{AI} = \frac{[CO_2]}{[CO_2]^{int}}, \quad \Phi_{BI} = \frac{[R1R2NH]_l}{C_r}
\] \hspace{1cm} (11)

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

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

\[at \xi = 0, \Phi_{AI} = 0\]

\[\Phi_{BI} = 1 \text{ for any } 1 \geq \xi \geq 0\]

\[at \xi = 0, \left. \frac{\partial \Phi_{AI}}{\partial \xi} \right|_{\xi=0} = 0\]

(14)
\[ |\frac{\partial \Phi_{Bi}}{\partial \xi} \bigg|_{\xi=1} = 0 \text{ for any } 1 \geq \zeta \geq 0 \]  

(15)

at \( \xi = 1 \)

\[ \frac{\partial \Phi_{Al}}{\partial \xi} \bigg|_{\xi=1} = \frac{Sh_{ext}}{2} \left[ 1 - \Phi_{Al} \xi=1 \right] \]  

(16)

\[ |\frac{\partial \Phi_{Bi}}{\partial \xi} \bigg|_{\xi=1} = 0 \text{ for any } 1 \geq \zeta \geq 0 \]  

(17)

\[ Gr_A = \frac{\bar{v}_z d_i^2}{l D_{CO_2}}, \quad Gr_B = \frac{\bar{v}_z d_i^2}{l D_{B_i R_2 NH}} \]  

(18)

\[ \beta_1 = \frac{L_{K_2 C_i}}{\bar{v}_z} \quad \beta_2 = \frac{L_{K_2 m[CO_2]g}}{\bar{v}_z} \quad \beta_3 = \frac{k - z}{k_{B_i C_T}} \quad \beta_4 = 4 k_{eq} m[CO_2]g \]  

(19)

\[ \frac{k_A g d_g}{D_A g} = 1.8 \left( \frac{d_g}{l} \right)^{0.92} \left( \frac{d_g \bar{v}_z}{v_{Ag}} \right)^{0.92} \left( \frac{v_{Ag}}{D_A g} \right)^{0.92} \]  

(20)

\[ \Phi_{Al} = 4 \int_0^1 \xi(1 - \xi^2) \Phi_{Al} d\xi \]  

(21)

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

(22)

\[ \eta_{CO_2} = \frac{[CO_2]_{li} - [CO_2]_{lo}}{[CO_2]_{li}} = 1 - \Phi_{Al} \]  

(23)
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\textsubscript{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\textsubscript{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\textsubscript{2}) before proceeding onto the stripper where the CO\textsubscript{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\textsubscript{2}. The process employs structured packing in the flue gas water cooler and CO\textsubscript{2} 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:

<table>
<thead>
<tr>
<th>Flue gas feed</th>
<th>132500 NM\textsuperscript{3}/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas temp.</td>
<td>180\textdegree C</td>
</tr>
<tr>
<td>Flue gas temp. inlet absorber</td>
<td>40\textdegree C</td>
</tr>
</tbody>
</table>
Flue gas press. : 615 mm WC
Lean solution flow rate : 195 ton/hr
CO₂ flow rate : 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 CO₂ 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.

**Table 3: CO₂ recovery vs. pressure**

<table>
<thead>
<tr>
<th>#</th>
<th>Press, mm WC</th>
<th>Product CO₂ flow, tons/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>set 1</td>
<td>265</td>
<td>11.4</td>
</tr>
<tr>
<td>set 2</td>
<td>267.7</td>
<td>11.8</td>
</tr>
<tr>
<td>set 3</td>
<td>436</td>
<td>14.2</td>
</tr>
<tr>
<td>set 4</td>
<td>456</td>
<td>17.17</td>
</tr>
<tr>
<td>set 5</td>
<td>468.4</td>
<td>17.2</td>
</tr>
<tr>
<td>set 6</td>
<td>454</td>
<td>17.23</td>
</tr>
<tr>
<td>set 7</td>
<td>453</td>
<td>17.58</td>
</tr>
<tr>
<td>set 8</td>
<td>457</td>
<td>17.68</td>
</tr>
<tr>
<td>set 9</td>
<td>615</td>
<td>18.80</td>
</tr>
</tbody>
</table>
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.
Table 4: CO2 recovery vs. temperature

<table>
<thead>
<tr>
<th>#</th>
<th>Temp., °C</th>
<th>Product CO2 flow, tons/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set1</td>
<td>55.2</td>
<td>11.4</td>
</tr>
<tr>
<td>set 2</td>
<td>54.7</td>
<td>11.8</td>
</tr>
<tr>
<td>set 3</td>
<td>56.8</td>
<td>14.2</td>
</tr>
<tr>
<td>set 4</td>
<td>59</td>
<td>17.17</td>
</tr>
<tr>
<td>set 5</td>
<td>61.5</td>
<td>17.2</td>
</tr>
<tr>
<td>set 6</td>
<td>61</td>
<td>17.23</td>
</tr>
<tr>
<td>set 7</td>
<td>61.3</td>
<td>17.58</td>
</tr>
</tbody>
</table>

**Temperature vs. CO2 recovered**

![Graph showing temperature vs. CO2 recovered](image)

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 CO2 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 CO2 component.
Table 5: CO2 recovery vs. gas flow rate

<table>
<thead>
<tr>
<th>Gas flow rate, NM³/HR</th>
<th>Product CO2 flow, tons/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>set 1 82007</td>
<td>11.4</td>
</tr>
<tr>
<td>set 2 92561</td>
<td>11.8</td>
</tr>
<tr>
<td>set 3 108702</td>
<td>14.2</td>
</tr>
<tr>
<td>set 4 110983</td>
<td>17.17</td>
</tr>
<tr>
<td>set 5 107187</td>
<td>17.2</td>
</tr>
<tr>
<td>set 6 110685</td>
<td>17.68</td>
</tr>
</tbody>
</table>

Gas Flow Rate vs. CO2 recovered

Fig. 4 Gas flow rate versus CO2 recovered

Effect of Solvent flow rate

Again, as could be expected, the increase in the solution flow rate improves the recovery of CO2 from the incoming gas (Table 6, Fig.5). The rise in CO2 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, CO2 recovery increases with the rise in solution flow rates but only to the extent as per the margins available on the CO2 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 CO2
where the recovery is possible by the partial pressure limit (fraction component in the incoming gas).

Table 6: CO2 recovery vs. solvent flow rate

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

Solvent Flow vs. CO2 recovered

Fig. 5 Solvent flow rate versus CO2 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.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibers material</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Fiber inner diameter (μm)</td>
<td>330</td>
</tr>
<tr>
<td>Fiber outer diameter (μm)</td>
<td>360</td>
</tr>
<tr>
<td>Fiber thickness (μm)</td>
<td>15</td>
</tr>
<tr>
<td>Average pore size r_p (μm)</td>
<td>0.06</td>
</tr>
<tr>
<td>Porosity ε</td>
<td>0.6</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>1930</td>
</tr>
<tr>
<td>Active module length (mm)</td>
<td>200</td>
</tr>
<tr>
<td>Inner contact area (m²)</td>
<td>0.40</td>
</tr>
<tr>
<td>Outer contact area (m²)</td>
<td>0.4363</td>
</tr>
</tbody>
</table>

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 CO₂ concentration decreases with the increase in the radius, since CO₂ 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 CO₂, by contrast, the amine concentration increases with the increase in the radius, since amine is flowing in the tube side.

Fig. 6 Dimensionless CO₂ 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 to 10 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.

![Graph showing the effect of liquid velocity on amine concentration](image)

Fig. 9 Effect of liquid velocity in the fiber lumen on Amine 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 $10^3$ mol/m$^3$. 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$_2$ 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


ملخص

يعتبر بأن ظاهرة الإحتباس الحراري العالمي وتغيير المناخ سبب الرئيسي إبعادات الغازات الدفيئة. ويعتبر ثاني أكسيد الكربون العامل الرئيسي في تغير المناخ العالمي الذي يؤدي مباشرة إلى مشاكل بيئية خطيرة. إن نصف مصادر أكسيد الكربون من نشاط الإنسان نتيجة إحراق الوقود الأحفوري في المصانع ومحطات توليد الطاقة في جميع أنحاء العالم. ويمكن دراسة عملية إمتصاص ثاني أكسيد الكربون من الغازات الخارجية من المداخل باستخدام أداة إمتصاص تقليدية وأغشية نسيجية بوليميرية معزوفة. ويتم مقارنة بيانات أداة الإمتصاص الصناعية بالبيانات الظاهرة باستخدام الأغشية النسيجية المعزوفة عبر طريقة حزمة برامج النظام العام لتمثيل العمليات. وفي هذا التحليل، مع تدفق محلل الإمتصاص في الجانب الداخلي من التحويل النسيجي والغاز النقي في نموذج يعمل بطريقة غير رطبة وتتم حل المعادلات التفاضلية الجزئية غير الخطية المزدوجة المستمدة من خلال طريقة الفروق الخفيفة المحدودة. ويستعمل ثاني أكسيد الكربون المنتج المخرج وادراسته من حيث سرعة السائل والتركيز الأولي للأملاح والمعامل الخارجي لنقل الكتلة. كما يشمل التحليل أثر قطر وطول الألياف على تركيز الغاز الخارجي كنتيجة لسرعة م دور السائل. وقد تبين أن سرعة السائل والتركيز الأولية للإمتصاص وكذلك الفن في الداخل وطول الألياف لها أكبر الأثر على عملية إزالة ثاني أكسيد الكربون.
شكر وتقدير

أود أن أعرب عن عميق شكري وإمتانني للدكتور نايف جاسم الذي أشرف على أطروحتي وزودني بملاحظاته واقتراحاته القيمة، كما أود أن أشكر منسق برنامج الماجستير الأساتذة الدكتور عبد الرزاق زكري على لطفه وتشجيعه ومساعدته المستمرة خلال فترة دراستي، وأتوجه بجزيل الشكر إلى الأساتذة كمال مصطفى والأستاذ طارق فارس على موافقتهما للإضمام 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 الاحتراق

إعداد
محمد راشد البراشد

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