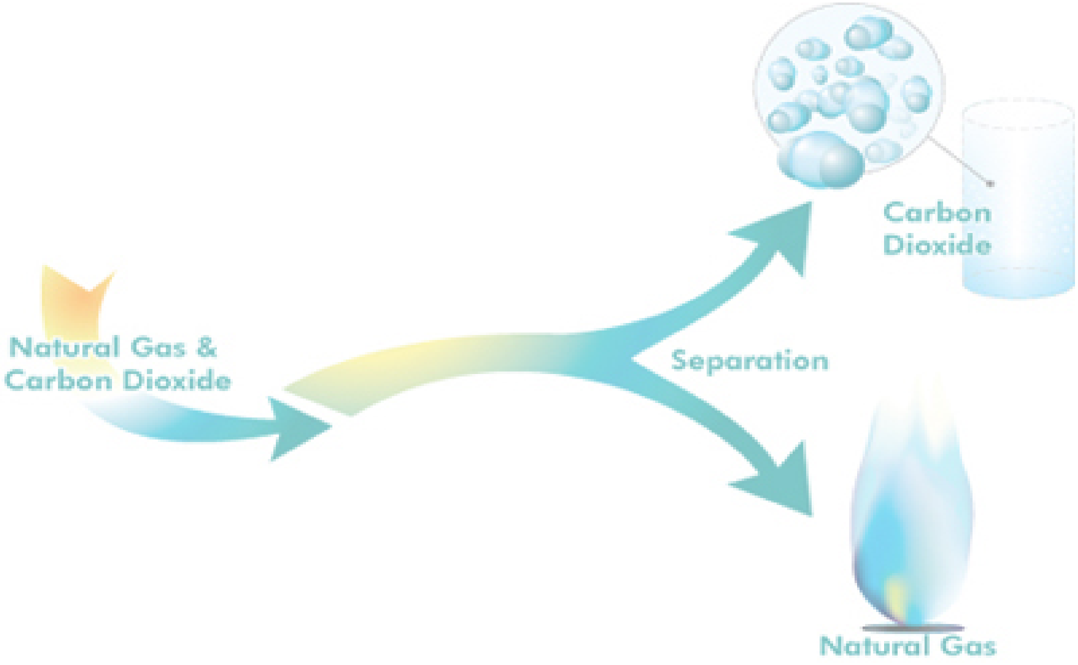
AALBORG UNIVERSITY
STUDENT REPORT

# Separation and Re-Injection of CO2 in Enhanced Oil Recovery Processes

## Master Degree in Oil and Gas Technology

## 10th semester – Group K10og-1-E14



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# Title page

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# Abstract

The current project focuses on the Carbon Dioxide Enhanced Oil Recovery injection including the methods for transporting the $CO_2$ to the platform, injection and production, as well as separation of the $CO_2$ and its recycling back to the reservoir.

The reservoir chosen is relatively a small one and is composed of heavy oil. Water flooding primary production has taken place for 9 years and approximately 22% of the original oil in place has been produced. For the further development of the field a $CO_2$-EOR continuous miscible injection was chosen. It is estimated that 263 000 kg/d would be injected a day and the life of production would take place for 18 years.

The estimated period of production has been divided into three stages – first 5 years of production, second 5 years and third 5 years of production. In this way a comparison between the different stages of production can be made. The production composition was calculated based on the initial composition, after the water flooding, and on the remaining oil and water in the reservoir.

With a known production properties for each stage of production, simulations with two different methods were made. The first method is amine gas sweetening, which is a well-known and widely used in the oil and gas industry. All three simulations gave very good results for the separation of $CO_2$ from the gas stream and further on for the recycling of it. On the other hand, the second method using ionic liquids, gave very unsatisfying results. Some of the reasons are due to the fact that Aspen Hysys (the software used for making the simulations) does not include any ionic liquid components in its database and the hypothetical components were not designed with all necessary properties.

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# 1. Introduction

Enhanced oil recovery (EOR) is a term used to describe a set of processes intended to increase the production of oil beyond what could normally be extracted when using conventional oil production techniques. In the best case scenario, by using traditional oil production methods, from 35 to 45% oil could be recovered from the original oil in place. Therefore, different techniques should be implemented, such as EOR, so that an additional 5 to 15% of oil could be produced.

There are three stages in the oil recovery. They are typically grouped in three categories, based on when they are likely to be implemented in a typical oilfield. The first one is called primary, the second one secondary and the last one tertiary oil recover (*Figure 1.1)*.

1. Primary recovery techniques are usually applied during the initial production phase of an oilfield. During this stage, the oil is driven to the surface by exploiting the pressure within the reservoir and using pumps. The pressure difference developed between the reservoir and the oil producing well, forces the oil to flow towards the well and from there to the surface. This is called reservoir drive. When the reservoir drive diminishes (as a result of oil and gas extraction) the primary recovery method is no longer viable. Hence, the secondary recovery method should be applied.
2. Secondary recovery techniques rely on the supply of external energy into the reservoir in the form of injecting fluids to increase reservoir pressure. Said in other words, replacing or increasing the natural reservoir drive with an artificial drive. This is typically achieved by injecting water (also known as water flooding) using a number of injecting wells. Other fluids that are injected during this stage are gases such as natural gas, air and others. The end of this stage is dictated by economic criteria.
3. The last stage – tertiary oil recovery – marks the end of life of an oilfield. As stated above, during this stage additional 5 to 15% of oil could be produced. This last stage is often called and also known as Enhanced Oil Recovery. There are numerous EOR methods that are known and used, but in this project the emphasis will be put on the $CO_2$-EOR method. Everything regarding this method will be explained further on in the project.

[3][4][5]

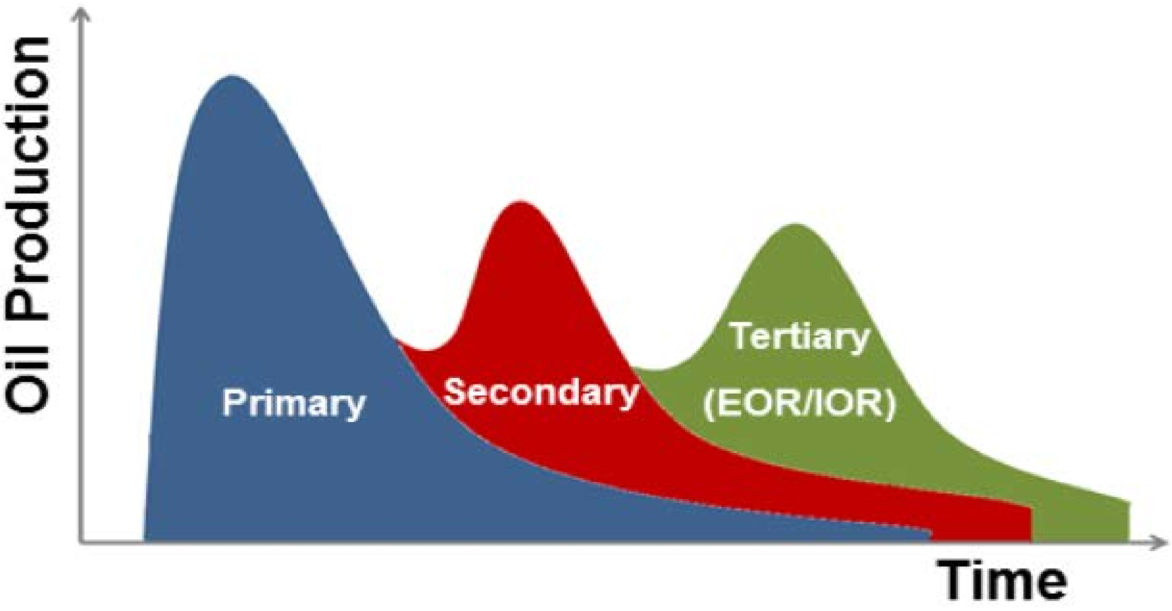


Figure 1.1 – Oil production stages [2]

For this project a field with heavy oil was chosen. Due to this fact there is not a natural drive, in order to produce crude oil. Therefore, the primary production of this field was implemented with the use of water flooding. The production using water flooding has taken place for around 9 years and approximately 22% of crude oil was produced.

In such cases the natural development of the field is to continue with Carbon Dioxide injection. It was estimated that $CO_2$-EOR continuous miscible injection will take place for approximately 18 years. The injection flowrate of $CO_2$ is taken to be 263 000 kg/d for a day.

The estimated period of production has been divided into three stages, which are as follows:

- First 5 years of production;
- Second 5 years of production;
- And finally third 5 years of production.

In this way a comparison between the different stages of production can be made. The production composition was calculated based on the initial composition, after the water flooding, and on the remaining oil and water in the reservoir.

The main focus of the project was put on the separation and recycling of the Carbon Dioxide produced. With a known production properties for each stage of production, simulations with two different methods were made. The first method is amine gas sweetening and the second method is using ionic liquids. The software used for the implementation of the simulations was Aspen Hysys V7.3 with a license provided by Aalborg University.

# 2. Enhanced Oil Recovery Technique Based on the $CO_2$

Enhanced Oil Recovery (EOR) is frequently defined as tertiary oil recovery process. Its main purpose is to extend the life of unprofitable or depleted fields. It is the final technique for extending the field's productive life, otherwise the oilfield should be abandoned. There are currently numerous EOR methods, which divided in categories are thermal, chemical, gas injection and other (e.g. microbial, acoustic and electromagnetic). The choice of the method and the expected recovery depends on many considerations, economic as well as technology. In this project the focus will be on gas injection method and most specifically – Carbon Dioxide gas injection. [7][8]

$CO_2$-EOR is currently the most attractive tertiary recovery method. It was first tried in 1972 in Scurry County, Texas. Since then it is extensively used in the US on onshore oilfields and in the recent years on offshore shallow water oilfields. Therefore, regulatory standards, business models and supply chains for $CO_2$-EOR in US are well established. Currently, there are more than 4 800 kilometers of $CO_2$ pipeline network infrastructure across South-East US. This extensive pipeline infrastructure is supplying many oilfields, which are in their final stage, with Carbon Dioxide, so that they can continue producing oil with $CO_2$-EOR technique. A map with the current $CO_2$-EOR projects in US is presented in the next figure. [7][8]

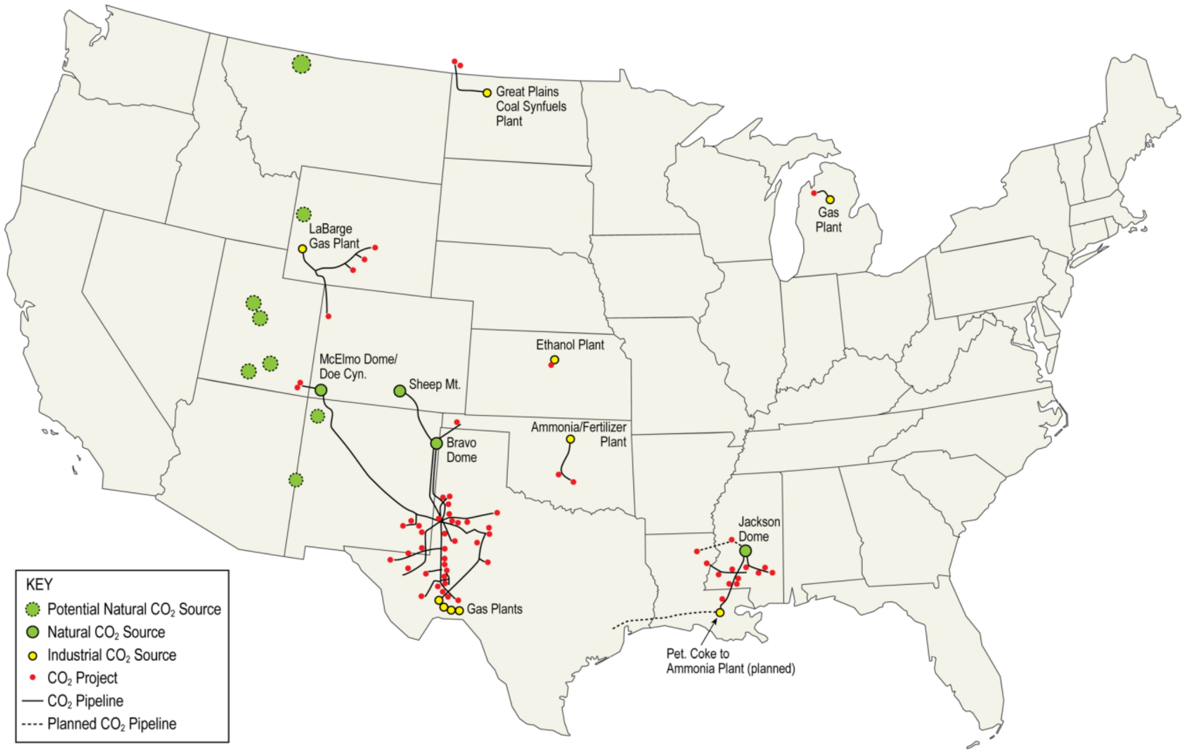


Figure 2.1 Location of current $CO_2$-EOR projects and pipeline infrastructure [36]

There are several reasons why this EOR method is so accessible for the oil and gas companies and they are as follow.

- First of all, most of the $CO_2$ that is used in the US oilfields is taken from naturally-sourced $CO_2$ reservoirs and just a few from power and industrial plants using Carbon Capture and Storage (CCS) system.
- Secondly, most of the oilfields are situated onshore, where the terrain is relatively flat, which reduces the need of expensive pipeline projects.
- Lastly, the drilling costs for onshore oil production projects are not as high as for offshore projects.

Taking in consideration all these facts, it is understandable the absence of specific offshore $CO_2$-EOR project in the North Sea.

Even though there is not a running offshore $CO_2$-EOR project in the North Sea that does not mean that there are is not a significant experience relevant to offshore $CO_2$ injection.

- Firstly, since 1997 in UK, Statoil has been separating the Carbon Dioxide from the produced natural gas mixtures offshore and re-injecting the separated gas using horizontal wells into an aquifer in the North Sea for long term storage.
- Secondly, at Snøhvit (Norway) oilfield, the separated $CO_2$ is transported from onshore with a pipeline to the offshore platform, so that the gas can be injected into an aquifer with the use of vertical wells.

[3][6]

## 2.1 $CO_2$-EOR Specifications and Use

The Carbon Dioxide EOR technique falls to the gas EOR method. This method is also recognized as solvent flooding, miscible-gas flooding or simply gas flooding. The injectant can be dry gas, enriched gas (such as hydrocarbon miscible), nitrogen, flue gas or as in this project – $CO_2$. [8]

Gas flooding method recovers oil by mass transfer. There are two types of mass transfer – the first one, is from the crude to the solvent (vaporizing gas drive) and the second one is from the solvent to the crude (condensing or rich gas drive). The Carbon Dioxide method falls to the first category, which means that is vaporizing gas drive. [3]

When the $CO_2$ is injected in the reservoir it interacts chemically and physically with the oil contained in the reservoir rock, creating favourable conditions that improve oil recovery. These conditions include:

- “The reduction of the capillary forces that inhibit oil flow through the pores of the reservoir by reducing the interfacial tension between oil and reservoir rock” [4]

- Oil swelling, which refers to expansion of the volume of the oil, and the subsequent reduction of its viscosity
- The oil's fluidity increases, because of the development of favourable complex phase
- "The maintenance of favourable mobility characteristics for oil and $CO_2$ to improve the volume sweep (replacement) efficiency" [4].

The Carbon Dioxide as a gas has the tendency to move faster than the oil within the reservoir. For $CO_2$-EOR to be effective, the oil's mobility (the ratio of effective permeability to phase viscosity) and that of the Carbon Dioxide must be similar. The effective permeability (the capability of a rock to allow passage of fluids through it) and viscosity (the extent to which a fluid resists a tendency to flow) are the main factors for the mobility of each phase. In general, when the mobility ratio between $CO_2$ and oil increases the volumetric sweep efficiency decreases. Furthermore, when the mobility ratio is larger than unity, fluid flow becomes unstable and the displacement front becomes non-uniform. As a result the Carbon Dioxide may by-pass the oil bank reaching the producing well before the oil does, because it does not sweep the maximum possible volume of the reservoir. [3][4][8]

Two processes have been developed for the $CO_2$-EOR: miscible and immiscible displacement. Depending on the reservoir's conditions the most suitable process may be chosen. These two $CO_2$-EOR processes are described in the next subchapter.

## 2.2 Miscible and Immiscible $CO_2$-EOR Processes

**Miscible.** Supercritical Carbon Dioxide can become miscible with petroleum, when there are satisfactory reservoir pressure and temperature conditions and crude oil composition. In other words, crude oil and $CO_2$ mix in all proportions forming a single fluid phase. As a result of the interaction between the crude oil and the $CO_2$, the oil swells (its volume increases), its viscosity is reduced and the surface tension effect diminishes, forcing the oil to flow out of the reservoir.

However, just because Carbon Dioxide forms a single phase with the oil under specific conditions, does not mean that it is instantaneously miscible with the oil at first contact. After the $CO_2$ is injected into the reservoir the miscibility conditions develop dynamically via composition changes. The process when the oil in place interacts with the injected Carbon Dioxide is called Multiple Contact Miscibility (MCM). As a result from the contact between the $CO_2$ and the crude oil, the Carbon Dioxide's composition is enriched with vapourised intermediate components of the oil. This specific change in the composition of the oil enables the miscibility between the oil and $CO_2$ (in other words vapourising process) forming a miscible zone between the oil bank and the injected $CO_2$.[3][4]

Pressure is the main factor for the miscibility of $CO_2$ in crude oil. In order for the Carbon Dioxide and the petroleum to become fully miscible a MMP is required. When such pressure is present, the density of $CO_2$ is similar to that of the crude oil. There are also certain criteria on which the minimum miscibility pressure (MMP) depends and they are – composition of the crude oil, purity of Carbon Dioxide and finally temperature in the reservoir. Furthermore, ”a miscible $CO_2$ displacement technique can only be implemented when $CO_2$ can be injected at a pressure higher than that of MMP, which in turn must be lower than the reservoir pressure” [4] *Figure 2.2* These conditions are typically achieved at depths greater than 700 m (valid for oil reservoirs in the North Sea). [4]

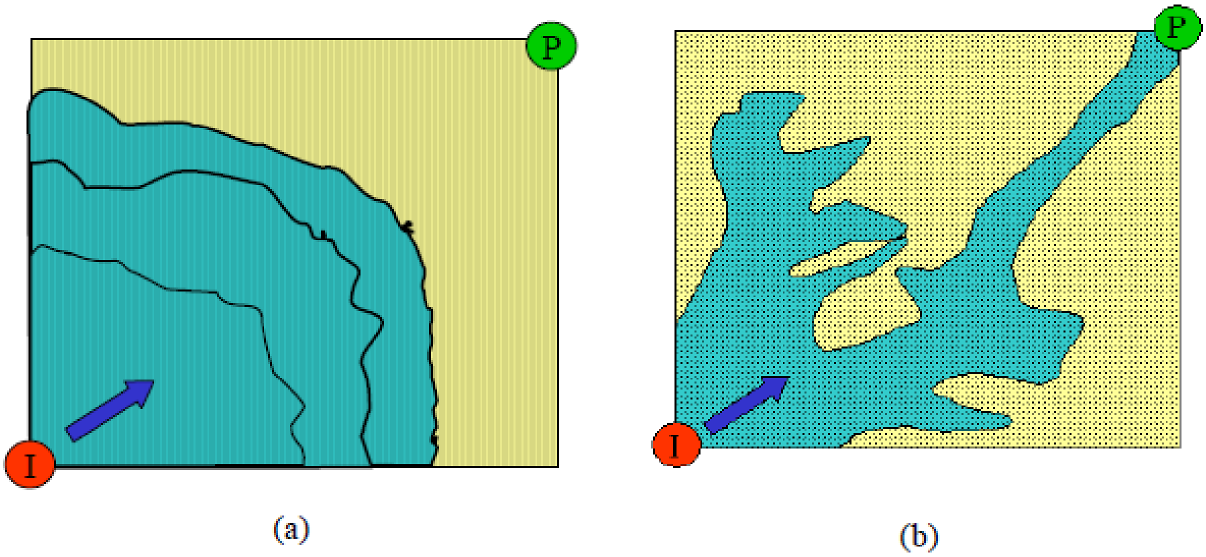


Figure 2.2 a) A stable front between the injected $CO_2$ and the oil, ensures the complete sweep of the reservoir maximizing recovery; b) Viscous fingering, results in the breakthrough of $CO_2$ leaving large volumes of the reservoir unaffected by the injection of $CO_2$. *[9]*

In theory, the whole oil from the reservoir can be recovered after it gets in contact with the $CO_2$. However, in practice, the usual recovered percentage is 5 to 15% (20% in the best cases). Some of the reasons that affect oil recovery are:

- Before a full miscibility is achieved, there is a need for a finite distance for the Carbon Dioxide to flow through the reservoir;
- Unstable flow, which leads to oil trapping, because the $CO_2$ is the easier flow in the reservoir compared to that of the oil in place;
- Unstable flow can also result in early breakthrough of $CO_{2;}$
- The need of $CO_2$ to mobilize also some water in the reservoir, which has been left after the second recovery stage using water flooding.

[4]

**Immiscible.** Carbon Dioxide can be injected into a reservoir and can be used as an oil recovery method even when the MMP is not reached. Such cases may be low pressure oil reservoirs or heavy oils. Under the stated conditions, the Carbon Dioxide does not become fully miscible with the oil, but it still partially dissolves in it and causes some swelling.

In immiscible displacement, the role of $CO_2$ is similar to that of water in water flooding method. In other words the role of $CO_2$ is to raise and maintain the reservoir's pressure. When both methods are compared it can be concluded that the water flooding offers higher recovery efficiencies (15-30%), but the Carbon Dioxide is used in limited number of projects to raise reservoir's pressure, and only when the permeability of the reservoir rock is too low or the geologic conditions do not favour the use of water.

$CO_2$ is typically injected at the crest of the reservoir at slow rates, aiming at filling the pore volume of the reservoir rock. In this way the injected gas creates an artificial gas cap, pushing the oil downwards and towards the producing wells *Figure 2.3*. Such process may not be as effective as it could be if it is applied after significant waterflooding. The reason is because the presence of water within the reservoir reduces the effectiveness of the process as it inhibits oil flow.

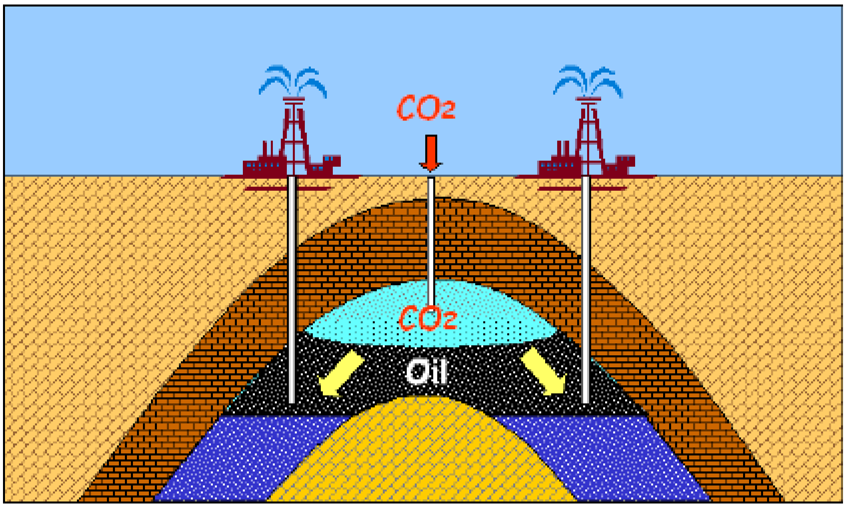


Figure 2.3 A schematic of the immiscible displacement technique [10]

The immiscible displacement process has not been very extensively used so far, due to being economically unmet. For example, much more significant amount of $CO_2$ is necessary; many new wells must be constructed, slow recovery timing. In some cases up to 10 years are needed before starting the production of recovery oil. Furthermore, an immiscible project is typically implemented in the whole reservoir, and it cannot be used for smaller scale implementation.

## 2.3 Summary

The summary for this chapter is as follows:

- The Enhanced Oil Recovery method is a tertiary recovery method. It is the final stage before abandoning the current oilfield. There are numerous EOR methods and the one that would be revised in details in this project is $CO_2$-EOR method.
- $CO_2$-EOR is being used for decades in the United States for producing more oil. Its main use is for onshore oilfields, but in the recent years a breakthrough is being made in the shallow waters of Gulf of Mexico, as well as some deep water oilfields.
- There aren’t any $CO_2$-EOR projects currently running in Europe’s richest oil and gas region – North Sea. The main reasons are economical, such as – availability of CO2 at low cost; necessity of pipeline from onshore power plant to the offshore rig; etc.
- $CO_2$-EOR method recovers oil by mass transfer. More specifically the mass transfer occurs from the crude to the solvent ($CO_2$) and is called vaporizing gas drive. When the Carbon Dioxide is introduced into the reservoir it interacts with the oil in place physically and chemically. The result is reduction of the capillary forces that inhibit the oil flow, swelling of the oil; increase of the oil’s fluidity and finally improved volume sweep efficiency.
- There are two main processes of the $CO_2$-EOR method – Miscible displacement and Immiscible displacement.
- In order for the miscible displacement to be used favourable conditions must be reached, such as pressure, temperature and crude oil composition. When the petroleum in the reservoir mixes with the injected $CO_2$ they form a single liquid phase. Their interaction results in swelling of the crude oil and reducing its viscosity, while in the same time the surface tension effect diminishes. As a result the oil is forced to flow towards the production wells.
- The immiscible displacement process is used for oilfields with low pressure or with heavy oils in place. In this process, the $CO_2$ is injected in the crest of the reservoir at slow rates simulating gas cap and pushing the oil towards the production wells. The Carbon Dioxide only partly dissolves in the crude oil, which causes swelling. Immiscible displacement process can be compared to the water flooding method, because the $CO_2$ has a similar role as the water when water flooding method is used.

# 3. Barriers for the Implementation of $CO_2$-EOR

This chapter provides a brief description of the barriers for deploying a $CO_2$-EOR project in Europe and more specifically in North Sea. The main barriers are as follows – capture, transport, injection and processing infrastructure.

A limited number of oilfields are currently been exploited worldwide using Enhanced Oil Recovery technique based on Carbon Dioxide ($CO_2$-EOR). Most of these kinds of projects, completed and still running, are situated in USA. Unfortunately, there aren't any implemented $CO_2$-EOR projects in Europe, so far, due to the lack of favourable economic situation for investment. It is an unfavourable economic situation, because of the fact that the majority of the European oilfields are situated in the North Sea, in other words – offshore. The unavailability of low cost Carbon Dioxide offshore is the major barrier for the implementation of $CO_2$-EOR project in Europe. The significant distance to the European oil-rich regions from the shore (where some of the coastal power stations are situated), makes the whole operation of $CO_2$ capturing, transport and injection very costly. [37][38]

As already mentioned, US have very significant experience in the $CO_2$-EOR projects. Unlike, US who get most of their $CO_2$ from natural reservoirs, Europe needs to capture it from nearby anthropogenic sources, such as power plants. For example, in West Texas has 3900 km of an integrated Carbon Dioxide pipeline infrastructure, which delivers over 25 million tonnes of $CO_2$ a year. Due to the corrosiveness of the fluid the material of the pipelines is carbon steel. To prevent internal corrosion the water specification are very low (less than 0.5 $g/Nm^3$ $CO_2$). However, despite these specifications, in Europe the pipelines also need to be coated to prevent external corrosion by the marine environment. Additionally, a major issue is also the corrosion on the platform's iron infrastructure. After the $CO_2$ is delivered to the platform it is injected into the well, where it dissolves in water and produces carbonic acid, which is highly corrosive to carbon steels. Furthermore, the bottom of the injector wells, as well as the tubing and casing (that form the annular producer wells) are exposed to corrosion. [37][38]

There are currently many proposed projects for $CO_2$ pipeline infrastructure across the North Sea. The idea is to deliver Carbon Dioxide to numerous oilfields using anthropogenic $CO_2$ captured from coal-fired power plants located in Denmark and the UK, as well as industrial sources on the West Coast of Norway, *Figure 3.1* [39]

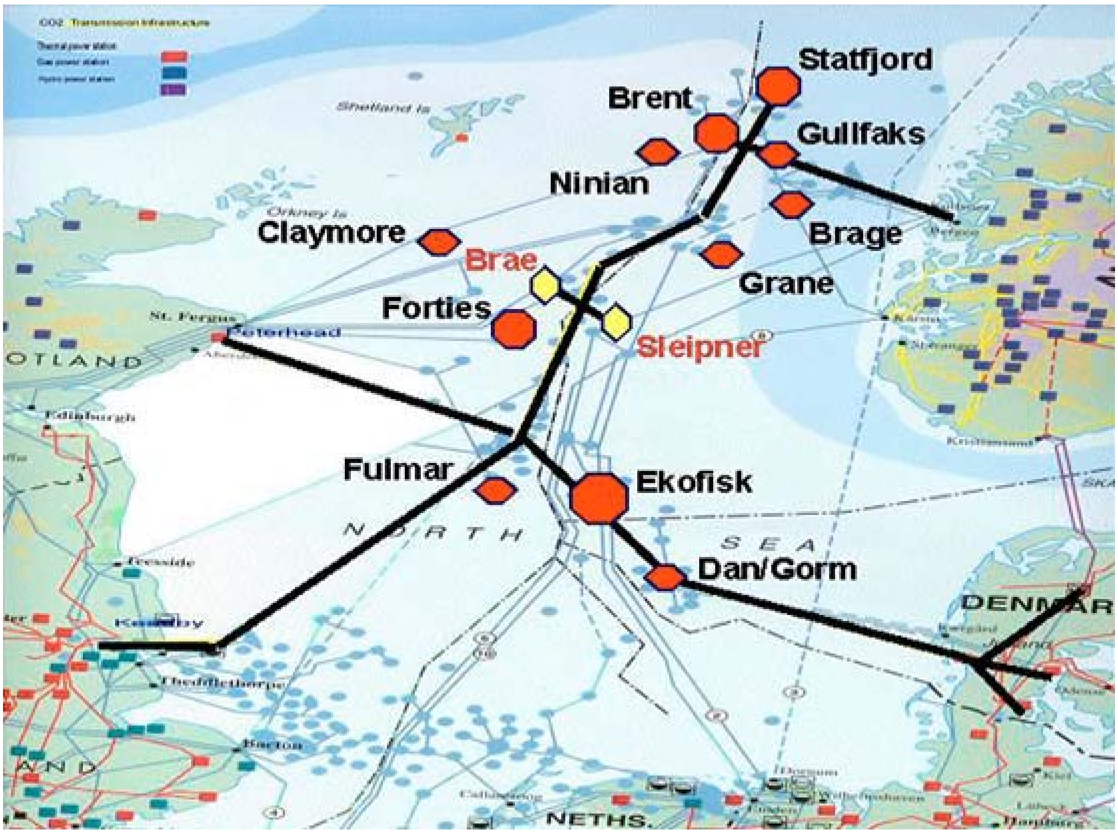


Figure 3.1 $CO_2$ pipeline infrastructure project [39]

None of these $CO_2$ pipeline infrastructure projects are yet implemented, due to the high initial capital cost. However, if at some point the oil prices stay at high level for long time the implementation of some of these projects will be started. [39]

Finally, there are some additional difficulties for the use of $CO_2$-EOR in the North Sea. One of them is the space and weight. As it is known these are very important aspects for the offshore platform, where the higher the weight the higher the cost of implementation. As an example the execution of $CO_2$ project will cause a new topside processing infrastructure which will increase the platform's weight. [37][38]

The last major issue that must be taken into consideration is the time deployment. In other words it is difficult to assess precisely when the EOR production will have to take place. Because the tertiary production process will take place for at least 10 years and it will be unprofitable and difficult to re-enter a field after abandonment to effectively implement an EOR project. [37][38]

# 4. Methods for the Separation of $CO_2$ from the Produced Fluids

After the barriers for the implementation of $CO_2$-EOR projects are described, in this chapter some of the methods for the separation of $CO_2$ will be introduced. Three different methods for the recycling of Carbon Dioxide are explained below. The first one is well-known and with a long history in the oil and gas production industry – *amine gas sweetening process.* The second one is also a popular method, which is getting more and more attractive due to the technologies development – *membrane separation process.* Finally, the most recent addition to the absorbent family, which is showing a great potential in the absorption of $CO_2$ with minimal environmental impact – *ionic liquids.*

## 4.1 Amine Gas Sweetening Process

Amines are compounds formed from ammonia ($NH_3$). They may be categorized by the number of hydrogen atoms bonded to the central nitrogen atom. For example, if one hydrogen atom is replaced with another hydrocarbon group, the result is a primary amine. If two hydrogen atoms are replaced the result is secondary amine and respectively, if three are replaced tertiary amines. The primary amines are the one that form the strongest bases, followed by the secondary and lastly the tertiary amines. Amines with stronger base form stronger chemical bonds and are more reactive to acid gases ($H_2S$ and $CO_2$).

The amines are used in aqueous solutions and their concentration ranges from 10 to 65 wt% (approximately). The physical properties of the amines used in this project can be seen in APPENDIX A. Most amines are alkanolamines, the difference between them is that the alkanolamines are with OH groups attached to the hydrocarbon groups and this way they reduce their volatility.

The process for removing acid gases from the sour gas can be introduced in two steps:

1. Physical absorption – the gas is dissolved in the liquid;
2. The weakly basic amines react with the weak acid (the dissolved gas).

[11][12]

For this project the primary amine - Monoethanolamine (abbreviated as MEA) is chosen for the recycling of $CO_2$ back to the reservoir. MEA is the most reactive amine for acid gas removal and is also the most basic one. It is toxic, flammable, colourless, corrosive and viscous liquid, where some of these are its main disadvantages. The molecular structure of MEA can be seen in the following figure [17]:

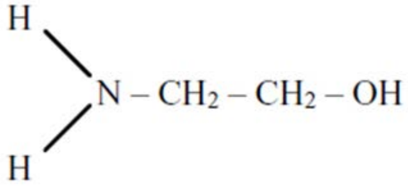


Figure 4.1 Molecular structure of MEA [11]

For many years the aqueous monoethanolamine solution has been used almost exclusively for the removal of hydrogen sulfide and carbon dioxide from natural gas. It has been used for all kinds of pressures (low, moderate and high), but with years it has been replaced by other more efficient amines for treating natural gases with high pressure. However, MEA is still a very good aqueous solution for removing acid gases from natural gas with low to moderate pressure. Besides the pressure criteria when choosing a solvent, another criteria such as the concentration of $CO_2$ in the treated gas, must be reviewed. For low to moderate concentrations of $CO_2$, MEA is capable of reducing it to level as low as 100 ppmv. This means that the treated gas would cover the pipeline specifications (for acid gases) and that almost all of the Carbon Dioxide would go for further treatment and reinjection into the reservoir. The aqueous monoethanolamine solution is removing both acid gases, but cannot be used for selective removal of H2S or CO2, when both of them are present in the treated gas. The concentration of MEA in the water solution is in the range between 10 to 20 wt%. Hence, for so many years the oil and gas industry uses the monoethanolamine, proving that 15 wt% is the most suitable concentration used. [13] [14] [15]

One of the advantages of MEA is its low molecular weight, which leads to high solution capacity at moderate concentrations, which makes it very useful for the complete removal of $CO_2$ and $H_2S$ with low to moderate concentration in the treated gas. Other advantages are its high alkalinity and the ease with which it can reclaim from contaminated solutions.[14] [17]

However, there are numerous disadvantages, such as the formation of irreversible reaction products with COS (carbonyl sulfide) and $CS_2$ (carbon disulfide). This leads to big chemical losses if the treated gas contains excessive amounts of these compounds. Another disadvantage is the relatively high vapour pressure, which leads to high vapourization losses. Moreover, the inability for selective removal of $CO_2$ and $H_2S$, when the other compound is present; higher corrosion rate than most other amines; and others. [14] [17]

In the next chapter a case study with three simulations will be introduced. With the use of MEA it will be found how effective this method is for the removing of $CO_2$. The three cases are with three different Carbon Dioxide concentrations – relatively low, moderate and high.

## 4.2 Membrane Separation Process

The most traditional method used to separate $CO_2$ from a gas stream is (as mentioned above) the amine absorption. However, there is another method, which keeps developing with time and is becoming more competitive for the separation of $CO_2$. This method is called membrane separation process. [18]

At the beginning membranes were restricted to small natural gas streams (with low content of $CO_2$) or to streams with very high $CO_2$ content, such as in EOR. Since 1980s gas separation with membranes has emerged into a commercially viable method. The membrane quality grew and this method/technology is applied to treat wider variety of natural gas streams. Nowadays, several hundreds of plants use membrane technology for the separation of gasses. [20][21]

Membrane based $CO_2$ separation processes are considered with a lot of incertitude, because of their sensitivity towards extreme process conditions, such as temperature (mainly), pressure and high flow rates. Hence, excluding these limitations the membrane separation technology offers a great potential for the separation of $CO_2$ due to the low capital investment, low energy requirement, small footprint, environmental friendliness, etc. In order to make an efficient design of membrane separation system a precise mathematical model should be implemented which will enable the accurate simulation of process variables and predict the required membrane area, energy and gas processing cost. [22]

A membrane is a barrier film that allows selective and specific permeation under conditions appropriate to its function. Gas separation membranes are based on the differences in physical or chemical interactions between gases and a membrane material. These specifications are the reason why one component passes through the membrane faster than another. Currently available are various types of gas separation membranes such as ceramic, polymeric and a combination of two (called hybrid). The separation of the gases relies on diffusivity and solubility of the gas molecules in the membrane. Therefore, differences in the partial pressure from one side of the membrane to other act as a driving force for gas separation.In *Figure 4.2* the process is shown. [19]

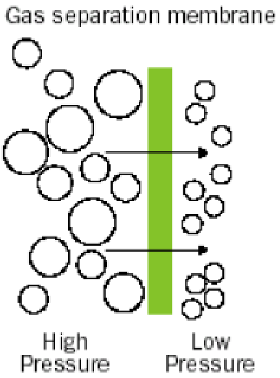


Figure 4.2 Principles of gas separation [19]

As already mentioned, in the last two decades, membrane separation processes have been widely used in various industrial branches. Nowadays, polymeric membranes dominate in the industrial applications. Therefore, an important field of research is currently held for the development of polymeric membranes, for even better performance. The research is consisted in the improvement of plasticization resistance that maintains selectivity and permeability, even at higher $CO_2$ partial feed pressures. [21][23]

The polymeric membranes feature some superior qualities over other membrane materials, such as lower cost, high performance separation and mechanical stability. The most frequently used mechanism is solution-diffusion, where gas molecules are transported through a polymeric membrane. Other mechanisms for separation include sieve effect and Knudsen diffusion. In order to understand the performance of a gas separation membrane the terms selectivity and permeability must be described. There appears to be a trade-off between the selectivity and permeability. There are gaps in the polymeric structure, where gas molecules tend to move through this free volume. “Because of the movement of the polymer chains, a channel between gaps can be formed allowing gas molecules to move from one gap to another and thus gas molecules can effectively diffuse through the membrane structure.” [23]. To achieve selective transport of gases a polymer which forms channels of a certain size, must be used. The explanation is that large channels will allow faster diffusion of gasses through a membrane at the cost of less selectivity. [23][24]

Based on the industry experience, if high $CO_2$ - high capture efficiencies are needed, a single-stage membrane system will not be enough. Therefore, for such cases a second membrane stage or even third are necessary.

## 4.3 Ionic Liquids

The third and final compound, for the separation of $CO_2$ that would be reviewed in this project is the ionic liquid (ILs). They are known from some time, but their extensive use as solvents for separation processes has recently become significant.

These compounds called ionic liquids are molted salts consisting of ions, such as anions and cations. Ionic liquids are salts that, unlike common salts, are liquid even at temperature below 100 °C or even at room temperature (room temperature ionic liquids, RTILs). This group of compounds can also be described with the terms – molten salt, liquid organic salt, nonaqueous ionic liquid and fused salt. Due to the immeasurably low vapour pressure, the ionic liquids are also known as Green Solvents. An important feature associated with ionic liquids is that their properties (such as conductivity, density, viscosity, gas solubility and others) can be tuned by varying the structure of the component ions to obtain desired solvent properties. As a result the ILs are also described as Designer Solvents. [25][26]

The first known attempts in the field of ionic liquids are from 1914, where Paul Walden has synthesized the first melting salt (ethylammonium nitrate[EtNH3]+[NO3]-) with melting point of 12 °C. Further on the aluminum chloride based molten salt was utilized as well as the melting salts with chloroaluminate ions for low temperature electroplating of aluminum. In 1980s and 1990s the low melting point ionic liquids were proposed as solvents for organic synthesis and became the most promising chemicals as solvents. Unfortunately, the ionic liquids in this period have been with limited application due to the fact that they were unstable to air and water. However, in 1992 the real interest to the ionic liquids began. The first stable to water and air ILs have been found - 1-n-butyl-3-methlyimidazolium tetrafluoroborate([bmim][BF4]) and 1-n-butyl-3-methlyimidazolium hexafluorophosphate ([bmim][PF6]). Since, this year (1992) more than 8000 scientific papers have been published and there are currently about 1 million simple ionic liquids that can be easily prepared in a laboratory by combination of different cations and anions. Currently, there are only around 300 ILs that are commercialized, which shows that there are almost unlimited opportunities in this field, which are still undiscovered. [25][26]

In the recent years, researchers keep developing the ionic liquids with the idea to replace the very well-known amine gas sweetening process. The process of separating acid gases from the gas stream using ILs is the same like with the amines – typical absorber/stripper process. The main drawbacks of the amines process is the high energy demand, solvent loss during the regeneration and corrosion during the whole process. However, the ionic liquids are considered (from the laboratory experiments) to have high $CO_2$ capture capacity, high solubility in water, thermal stability, negligible vapour pressure, tunable physic-chemical characteristic and low toxicity. [27][28]

In this project two Aspen Hysys simulations will be made. The first one will be with the ionic liquid tetramethylammoniumglycinate ([N1111][Gly])[26], which will be simulated in a solution with water. The second one, 1-butyl-3-methylimidazoliumtetrafluoroborate will be simulated as a pure component for the removal of $CO_2$ from the gas stream.

## 4.4 Summary

In this chapter three different methods, for the removal of Carbon Dioxide from a gas stream were reviewed. The first one, Amine Gas Sweetening, is the most mature, well known and widely used in the oil and gas industry. The second one, membrane separation, is constantly developing and is considered that it will become a very important method for the removal of $CO_2$. Finally the last one, ionic liquids, which are not a new compound group, but has recently (since 1992) become very interesting for the oil and gas industry. The interest is related to the discovery of new ionic liquids which are stable to air and water. Furthermore, researchers keep developing new ionic liquids to achieve maximum separation and hopefully low price.

In the following table some of the advantages and disadvantages of these three methods will be reviewed.

Table 4.1 Advantages and disadvantages of amine gas sweetening, membrane separation and ionic liquids [29]

| | **Advantages** | **Disadvantages** |
|---|---|---|
| **Amine Gas Sweetening** | 1. Well-understood technology, already implemented in large scale in different industries;<br>2. Suitable for retrofit;<br>3. Applicable to separation of CO2 at low concentrations;<br>4. Recovery rates of up to 95%;<br>5. Product purity >99 vol% | 1. Significant energy requirement due to solvent regeneration;<br>2. Solvent loss;<br>3. Degradation and equipment corrosion;<br>4. Environmental impacts due to solvent emissions;<br>5. Large absorber volume. |
| **Membrane Separation** | 1. No regeneration process;<br>2. Simple modular system;<br>3. No waste streams; | 1. Plug of membranes by impurities in the gas stream;<br>2. Non proven industrially |
| **Ionic Liquids** | 1. Low vapour pressure;<br>2. Non-toxicity;<br>3. Thermal stability; | 1. High viscosity;<br>2. High regeneration energy;<br>3. High unit costs. |

# 5. Case Study – Simulations and Results

In this chapter a case study for the removal of Carbon Dioxide from the production stream will be reviewed. The case study examines a heavy oil formation situated in continental USA, Texas. In a period of 9 years there has been a primary oil production with water flooding. During the water flooding, almost 22% of the original oil in place has been produced. As a further development a $CO_2$-EOR injection has been selected.

The reviewed reservoir is relatively small with 7.34 MMbbl (908 641 339 kg/d). During the water flooding 1.61 MMbbl (199 306 888 kg/d) have been produced. Furthermore, 13.9 MMbbl (2 205 476 441 kg/d) of water have been injected and 89% of it has been produced. In *Table 5.1* the well composition after the primary production can be reviewed, as well as a reservoir overview.

Table 5.1 Reservoir properties and well composition

| | |
|---|---|
| **Reservoir pressure** | 248.2 bar |
| **Reservoir temperature** | 92.22 °C |
| **Oil in place after primary production** | 709 300 000 kg/d |
| **Water in the reservoir after primary production** | 253 900 000 kg/d |

| **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** | **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** |
|---|---|---|---|---|---|
| $CO_2$ | 0,01 | 96 320 | $C_{14}$ | 2,46 | 23 694 720 |
| $H_2O$ | 26,36 | 253 900 000 | $C_{15}$ | 2,47 | 23 791 040 |
| $N_2$ | 0,34 | 3 274 880 | $C_{16}$ | 2,33 | 22 442 560 |
| $C_1$ | 10,43 | 100 461 760 | $C_{17}$ | 2,30 | 22 153 600 |
| $C_2$ | 0,43 | 4 141 760 | $C_{18}$ | 2,22 | 21 383 040 |
| $C_3$ | 0,47 | 4 527 040 | $C_{19}$ | 2,26 | 21 768 320 |
| $iC_4$ | 0,11 | 1 059 520 | $C_{20}$ | 2,10 | 20 227 200 |
| $nC_4$ | 0,29 | 2 793 280 | $C_{21}$ | 1,94 | 18 686 080 |
| $iC_5$ | 0,21 | 2 022 720 | $C_{22}$ | 1,76 | 16 952 320 |
| $nC_5$ | 0,38 | 3 660 160 | $C_{23}$ | 1,66 | 15 989 120 |
| $C_6$ | 0,80 | 7 705 600 | $C_{24}$ | 1,57 | 15 122 240 |
| $C_7$ | 0,99 | 9 535 680 | $C_{25}$ | 1,43 | 13 773 760 |
| $C_8$ | 1,44 | 13 870 080 | $C_{26}$ | 1,40 | 13 484 800 |
| $C_9$ | 1,85 | 17 819 200 | $C_{27}$ | 1,35 | 13 003 200 |
| $C_{10}$ | 2,18 | 20 997 760 | $C_{28}$ | 1,28 | 12 328 960 |
| $C_{11}$ | 2,27 | 21 864 640 | $C_{29}$ | 1,23 | 11 847 360 |
| $C_{12}$ | 2,34 | 22 538 880 | $C_{30}+$ | 16,86 | 162 395 520 |
| $C_{13}$ | 2,51 | 24 176 320 | **TOTAL** | **100** | **963 200 000** |

$CO_2$-EOR injection was selected for continuing the oil production. Continuous miscible $CO_2$ injection was estimated with an injection rate of 263 000 kg/d. It is considered that due to the small size of the reservoir the enhanced oil recovery production will take place for 18 years. In the following subpoints total of 6 simulations are made, where 3 of them use the amine gas sweetening process and the other 3 – ionic liquid compound. The simulations represent the average production of crude oil and $CO_2$ in:

1. The first five years of production;
2. The second five years of production;
3. And in the final five years of production.

In other words, the $CO_2$-EOR production life (18 years) is shown in three stages – 5 years; 10 years and 15 years (where the final 3 years are not taken in account). In this way the $CO_2$ production in each stage can be compared, as well as its separation and amount of Carbon Dioxide that is recycled back to the reservoir.

Amine gas sweetening process and process using ionic liquid have been selected in order to compare the old and well known amine process with the new and still not proven (in the oil and gas industry) ionic liquid process. The reservoir data used in the simulations for both processes is the same, so that the comparison to be realistic.

The simulations are made in Aspen Hysys (version 7.3) with a license provided by Aalborg University. This software is a special and valuable process simulator, which is recognized as one of the leading platforms for simulation and optimization in the oil and gas industry. The software provides engineers with flexible access to wide variety of tools and equipment, as well as the opportunity to achieve better design, investment decisions and to increase the efficiency of upstream projects.

## 5.1 Amine Gas Sweetening Simulations

In chapter 4, detailed information for the amines has been provided, as well as for the Monoethanolamine (MEA). MEA will be the amine used in the simulations for the removal of $CO_2$ from the gas stream. Furthermore, the $CO_2$ will be purified and prepared for recycling.

### 5.1.1 First Simulation (5 years of production)

Based on the initial data provided above and on the papers – [30][31][32][33][34] – which helped me to estimate the production composition and properties of this stage and the others.

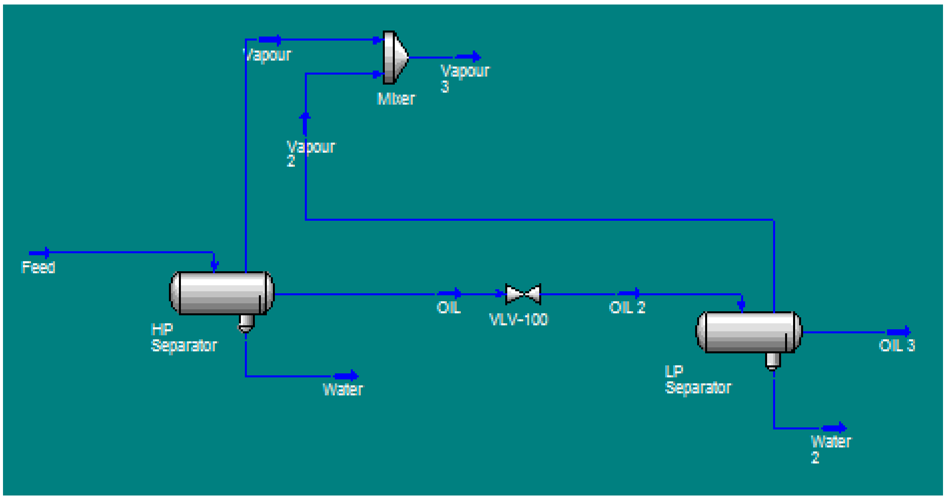
For this stage the following production properties and composition have been estimated.

Table 5.2 First stage production properties and composition

| | | | **Pressure** | 235 bar | |
|---|---|---|---|---|---|
| | | | **Temperature** | 83 °C | |
| **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** | **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** |
| $CO_2$ | 0,04 | 114 637 | $C_{14}$ | 3,09 | 5 290 711 |
| $H_2O$ | 20,40 | 34 918 568 | $C_{15}$ | 3,10 | 5 310 601 |
| $N_2$ | 0,36 | 616 210 | $C_{16}$ | 2,92 | 4 992 362 |
| $C_1$ | 5,41 | 9 259 583 | $C_{17}$ | 2,88 | 4 932 693 |
| $C_2$ | 0,23 | 386 158 | $C_{18}$ | 2,79 | 4 773 574 |
| $C_3$ | 0,24 | 419 023 | $C_{19}$ | 2,84 | 4 853 133 |
| $iC_4$ | 0,05 | 903 77 | $C_{20}$ | 2,64 | 4 515 005 |
| $nC_4$ | 0,15 | 254 700 | $C_{21}$ | 2,44 | 4 176 877 |
| $iC_5$ | 0,11 | 188 971 | $C_{22}$ | 2,21 | 3 779 079 |
| $nC_5$ | 0,20 | 336 861 | $C_{23}$ | 2,08 | 3 560 290 |
| $C_6$ | 0,42 | 714 804 | $C_{24}$ | 1,96 | 3 361 391 |
| $C_7$ | 0,51 | 879 126 | $C_{25}$ | 1,79 | 3 063 043 |
| $C_8$ | 0,74 | 1 273 501 | $C_{26}$ | 1,75 | 3 003 373 |
| $C_9$ | 0,96 | 1 643 227 | $C_{27}$ | 1,70 | 2 903 924 |
| $C_{10}$ | 2,73 | 4 674 124 | $C_{28}$ | 1,60 | 2 744 805 |
| $C_{11}$ | 2,86 | 4 892 913 | $C_{29}$ | 1,55 | 2 645 355 |
| $C_{12}$ | 2,94 | 5 032 142 | $C_{30}$+ | 21,17 | 36 239 380 |
| $C_{13}$ | 3,15 | 5 390 160 | **TOTAL** | **100** | **171 230 682** |

Following the information from the table above, the first stage simulation using MEA can be designed. The **Feed Stream** is designed with the composition given above and with a reduced pressure (to 70 bar) and temperature (to 43 °C). It was observed that there are 3 phases in the feed stream – vapour (mainly because of the methane), liquid (oil) and aqueous phase (water). Therefore, the feed stream enters a 3 phase high pressure separator. 3 streams are exiting the separator (gaseous, light liquid and heavy liquid). The light liquid stream goes through a valve to reduce the pressure to 20 bar and to enter a 3 phase low pressure separator for a final separation. The two gaseous streams coming out from the two separators are mixed into one stream with a mixer, so that it can enter the **Absorber**, *Figure 5.1*.

Figure 5.1 Separation of the 3 phase feed stream



The stream **Vapour 3** which is entering the absorber for removing the Carbon Dioxide is with the following mass flows:

Table 5.3 Mass flowrates of Vapour 3 stream

| **Component** | **Mass flowrate (kg/d)** |
|---|---|
| $CO_2$ | 84 681,19 |
| $H_2O$ | 19 219,81 |
| $N_2$ | 601 716,83 |
| $C_1$ | 8 585 721,93 |
| $C_2$ | 259 555,72 |
| $C_3$ | 163 368,12 |
| $iC_4$ | 20 139,79 |
| $nC_4$ | 46 002,24 |
| $iC_5$ | 17 745,44 |
| $nC_5$ | 25 905,95 |
| $C_6$ | 22 750,53 |
| $C_7$ | 11 685,96 |
| $C_8$ | 7 038,93 |
| $C_9$ | 3 893,43 |
| $C_{10}$ | 4 830,82 |
| $C_{11}$ | 2 155,13 |
| $C_{12}$ | 1 059,34 |

The **Absorber** is designed to be with 18 trays, as this was found to be the optimum number of trays for the best removal of $CO_2$. The operating pressure is at 70 bar and the temperature is kept at 43 °C, as it is known that with high pressure and lower temperature the sweetening process is more efficient. Finally, the MEA in solution with water (**MEA stream**) is with the following design:

- Pressure of 70 bar; Temperature of 48 °C;
- Mass flowrate – 2 001 137 kg/d;
- MEA – 11 wt% and $H_2O$ – 89 wt%;
- Enters from the top of the column.

Entering the given parameters the absorber converges and from the top of it exits the lean natural gas (with small amount of $CO_2$ and $H_2O$). From the bottom exits the so called **MEA Rich** (consisted mainly of water, MEA and $CO_2$, with traces from methane, ethane propane and others). After exiting the absorber the stream **MEA Rich** goes through a valve, where the pressure is reduced to 3 bar. From there it goes through a **Cross Heat Exchanger**, where is heated to 98 °C and it enters the **Regeneration Column**.

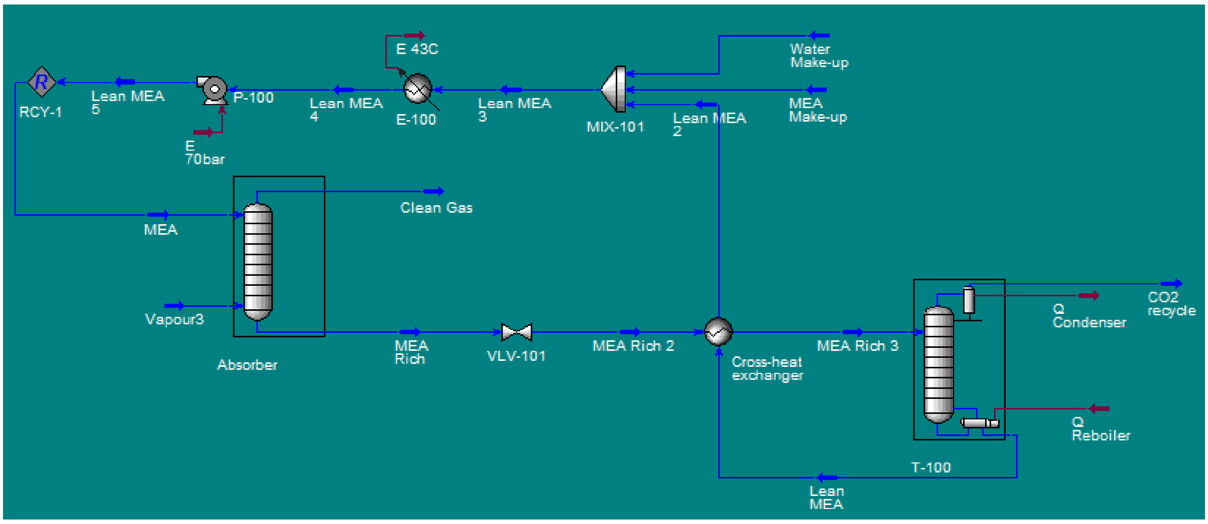
In the regeneration column the rich MEA stream will be purified from the contaminants, such as $CO_2$ and methane and it will be recycled to the absorber. On the other hand, the $CO_2$ will be recycled back to reservoir.

The optimum design of the regeneration column is found to be as follows:

- 17 stages with a small pressure drop of 1 bar;
- The condenser is designed to be with full reflux, pressure of 1 bar and temperature of 38 °C;
- The reboiler is with pressure of 2 bar and a duty of 3,700e+8 kJ/h.

From the bottom exits the **Lean MEA** stream which is composed mainly of $H_2O$, MEA and a very small amount of $CO_2$, which is negligible. During the process there are small losses of water and MEA, which should be fulfilled. Therefore, after the stream exits the cross heat exchanger it enters a **Mixer** where it mixes with the make-ups of water and MEA. Further on, it goes through a cooler and a pump, so that it meets the inlet properties and is recycled to the absorber. In *Figure 5.2* the whole process can be reviewed.

Figure 5.2 Amine Gas Sweetening Simulation



From the top of the regeneration column the separated Carbon Dioxide exits. From here it goes to a further treatment to meet the injection properties and is recycled to the reservoir. The composition of the stream **$CO_2$ recycle** can be seen in the following table.

Table 5.4 Recycled Carbon Dioxide composition

| **Pressure** | 1 bar |
|---|---|
| **Temperature** | 38 °C |
| **Component** | **Mass flowrate (kg/d)** |
| $CO_2$ | 84 324,3 |
| $H_2O$ | 2 629,9 |
| $N_2$ | 71,5 |
| $C_1$ | 1 869,5 |
| $C_2$ | 47,5 |
| $C_3$ | 20,2 |
| $iC_4$ | 0,1 |
| $nC_4$ | 0,2 |
| $iC_5$ | 0,1 |
| $nC_5$ | 0,1 |
| $C_6$ | 0,9 |
| $C_7$ | 6,2 |
| $C_8$ | 3,4 |
| $C_9$ | 1,5 |
| $C_{10}$ | 1,7 |
| $C_{11}$ | 6,3 |
| $C_{12}$ | 2,6 |
| **TOTAL** | **88 960** |

## SUMMARY

A simulation for the first 5 years of production with $CO_2$ injection was presented. The data with which the simulation was made is estimated as average for a day during the first 5 years of production. In the next *Table 5.5* a comparison of how much $CO_2$ is produced and how much is recycled can be seen.

Table 5.5 Produced Carbon Dioxide and recycled $CO_2$

| | |
|---|---|
| Produced Carbon Dioxide (for a day) | 114 637 kg/d |
| Recycled Carbon Dioxide (for a day) | 84 324 kg/d |
| Efficiency percentage | 74 % |
| Purity of the recycled $CO_2$ | 94.8 % |
| Carbon Dioxide injected (for a day) | 234 100 kg/d |

From the table above, it can be concluded that 74 % of the $CO_2$ produced for a day is separated and recycled to the reservoir. On the other hand, the purity of $CO_2$ achieved with MEA is 94.8 %. Finally, from the original $CO_2$ injected for a day during the first period of 5 years, 36 % of it is recycled back to the reservoir.

### 5.1.2 Second Simulation (10 years of production)

After the completion of the first stage simulation in this chapter a simulation for the second 5 years of production will be represented. The production properties and composition have been estimated and they can be seen in the following table.

Table 5.6 Second stage production properties and composition

| | | | **Pressure** | 228 bar | |
|---|---|---|---|---|---|
| | | | **Temperature** | 79 °C | |
| **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** | **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** |
| $CO_2$ | 0,13 | 192 700 | $C_{14}$ | 2,99 | 4 601 012 |
| $H_2O$ | 31,73 | 48 875 750 | $C_{15}$ | 3,00 | 4 621 191 |
| $N_2$ | 0,11 | 176 689 | $C_{16}$ | 2,82 | 4 338 673 |
| $C_1$ | 3,57 | 5 500 171 | $C_{17}$ | 2,78 | 4 278 134 |
| $C_2$ | 0,15 | 227 986 | $C_{18}$ | 2,70 | 4 157 054 |
| $C_3$ | 0,16 | 250 785 | $C_{19}$ | 2,74 | 4 217 594 |
| $iC_4$ | 0,03 | 51 297 | $C_{20}$ | 2,54 | 3 914 896 |
| $nC_4$ | 0,10 | 153 891 | $C_{21}$ | 2,36 | 3 632 378 |
| $iC_5$ | 0,07 | 113 993 | $C_{22}$ | 2,14 | 3 289 320 |
| $nC_5$ | 0,13 | 199 488 | $C_{23}$ | 2,00 | 3 087 521 |
| $C_6$ | 0,28 | 427 474 | $C_{24}$ | 1,90 | 2 926 082 |
| $C_7$ | 0,34 | 524 369 | $C_{25}$ | 1,73 | 2 663 744 |
| $C_8$ | 0,49 | 758 055 | $C_{26}$ | 1,70 | 2 623 076 |
| $C_9$ | 0,63 | 974 642 | $C_{27}$ | 1,65 | 2 541 740 |
| $C_{10}$ | 0,74 | 1 145 632 | $C_{28}$ | 1,56 | 2 399 403 |
| $C_{11}$ | 0,78 | 1 202 628 | $C_{29}$ | 1,50 | 2 318 067 |
| $C_{12}$ | 0,80 | 1 236 826 | $C_{30}+$ | 20,61 | 31 741 249 |
| $C_{13}$ | 3,04 | 4 681 731 | **TOTAL** | **100** | **154 045 240** |

Following the information from the table above, the second stage simulation using MEA can be designed. This simulation is with the same unit design as the one in the first stage. Therefore, just the design of the units and the streams will be presented, as well as the production data. The **Feed Stream** is designed with the composition given above and with a reduced pressure (to 70 bar) and temperature (to 43 °C). It was observed that there are 3 phases in the feed stream – vapour (mainly because of the methane), liquid (oil) and aqueous phase (water). Therefore, the feed stream enters a 3 phase high pressure separator and afterwards a 3 phase low pressure separator. The pressure before the second separator is reduced to 5 bar, so that the stream to flash and more $CO_2$ to be separated. The two gaseous streams coming out from the two separators are mixed into one stream with a mixer, so that it can enter the **Absorber**.

The stream **Vapour 3** which is entering the absorber for removing the Carbon Dioxide is with the following mass flows:

Table 5.7 Mass flowrates of Vapour 3 stream (second simulation)

| Component | Mass flowrate (kg/d) |
|---|---|
| $CO_2$ | 188 074,16 |
| $H_2O$ | 47 438,99 |
| $N_2$ | 174 682,88 |
| $C_1$ | 5 387 813,60 |
| $C_2$ | 197 263,27 |
| $C_3$ | 158 294,57 |
| $iC_4$ | 20 836,85 |
| $nC_4$ | 52 177,38 |
| $iC_5$ | 20 356,14 |
| $nC_5$ | 29 210,80 |
| $C_6$ | 24 447,20 |
| $C_7$ | 11 504,99 |
| $C_8$ | 6 312,28 |
| $C_9$ | 3 193,56 |
| $C_{10}$ | 1 508,52 |
| $C_{11}$ | 626,13 |
| $C_{12}$ | 288,44 |

The **Absorber** is designed to be with 18 trays, operating pressure of 70 bar and the temperature is kept at 43 °C. The MEA in solution with water (**MEA stream**) is with the following design:

- Pressure of 70 bar; Temperature of 48 °C;
- Mass flowrate – 3 516 000 kg/d;
- MEA – 13 wt% and $H_2O$ – 87 wt%;
- Enters from the top of the column.

Before **Mea Rich** stream enters the **Regeneration Column** the pressure is reduced to 3 bar and the temperature is increased to 98 °C. The column is designed to be with the following specifications:

- 18 stages with a small pressure drop of 1 bar;

- The condenser is designed to be with full reflux, pressure of 1 bar and temperature of 38 °C;
- The reboiler is with pressure of 2 bar and a duty of 5,100e+8 kJ/h.

From the bottom exits the **Lean MEA** stream which is composed mainly of $H_2O$, MEA and a very small amount of $CO_2$. The stream goes through the cross heat exchanger to exchange heat, from there to a mixer to add the make-up streams, afterwards cooler, pump and is recycled to the absorber.

From the top of the regeneration column the separated Carbon Dioxide exits. The composition of the stream **$CO_2$ recycle** can be seen in the following table.

Table 5.8 Recycled Carbon Dioxide composition

| **Pressure** | 1 bar |
|---|---|
| **Temperature** | 38 °C |
| **Component** | **Mass flowrate (kg/d)** |
| $CO_2$ | 187 973,05 |
| $H_2O$ | 5 780,78 |
| $N_2$ | 55,38 |
| $C_1$ | 3 157,74 |
| $C_2$ | 90,46 |
| $C_3$ | 50,13 |
| $iC_4$ | 0,34 |
| $nC_4$ | 0,81 |
| $iC_5$ | 0,38 |
| $nC_5$ | 0,53 |
| $C_6$ | 3,18 |
| $C_7$ | 0,20 |
| $C_8$ | 0,10 |
| $C_9$ | 0,04 |
| $C_{10}$ | 0,02 |
| $C_{11}$ | 0,01 |
| $C_{12}$ | 0,00 |
| **TOTAL** | **197 113,15** |

**SUMMARY**

In this subpoint the second stage simulation was made. This stage covers the second 5 years of production. As in the first simulation here again an average data for one day during these second 5 years of production have been estimated. A summary of the achieved results can be seen in the following table.

Table 5.9 Produced Carbon Dioxide and recycled $CO_2$

| | |
|---|---|
| Produced Carbon Dioxide (for a day) | 215 761 kg/d |
| Recycled Carbon Dioxide (for a day) | 187 973 kg/d |
| Efficiency percentage | 87 % |
| Purity of the recycled $CO_2$ | 95.36 % |
| Carbon Dioxide injected (for a day) | 257 800 kg/d |

From the table above, it can be concluded that 87 % of the $CO_2$ produced for a day is separated and recycled to the reservoir. On the other hand, the purity of $CO_2$ achieved for this simulation is a little higher than with the first one – MEA is 95.36 %. Finally, from the original $CO_2$ injected for a day during the second period of 5 years, 73 % of it is recycled back to the reservoir.

### 5.1.3 Third Simulation (15 years of production)

After the completion of the first and second stage simulation in this chapter the a simulation for the final stage of production will be made. This of course covers the third 5 years of production. The production properties and composition have been estimated and they can be seen in the following table.

Table 5.10 Second stage production properties and composition

| | | | **Pressure** | 219 bar | |
|---|---|---|---|---|---|
| | | | **Temperature** | 71 °C | |
| **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** | **Comp.** | **Mole Fraction (%)** | **Mass flowrate (kg/d)** |
| $CO_2$ | 0,24 | 287 740 | $C_{14}$ | 1,76 | 1 854 263 |
| $H_2O$ | 59,48 | 62 840 250 | $C_{15}$ | 1,76 | 1 854 263 |
| $N_2$ | 0,07 | 76 072 | $C_{16}$ | 1,65 | 1 744 380 |
| $C_1$ | 2,28 | 2 413 183 | $C_{17}$ | 1,64 | 1 730 645 |
| $C_2$ | 0,10 | 101 430 | $C_{18}$ | 1,59 | 1 675 704 |
| $C_3$ | 0,10 | 109 882 | $C_{19}$ | 1,61 | 1 703 175 |
| $iC_4$ | 0,02 | 25 357 | $C_{20}$ | 1,50 | 1 579 557 |
| $nC_4$ | 0,06 | 67 620 | $C_{21}$ | 1,38 | 1 455 940 |
| $iC_5$ | 0,05 | 50 715 | $C_{22}$ | 1,25 | 1 318 587 |
| $nC_5$ | 0,08 | 88 751 | $C_{23}$ | 1,18 | 1 249 910 |
| $C_6$ | 0,18 | 185 955 | $C_{24}$ | 1,12 | 1 181 234 |
| $C_7$ | 0,22 | 228 217 | $C_{25}$ | 1,01 | 1 071 352 |
| $C_8$ | 0,31 | 329 647 | $C_{26}$ | 0,99 | 1 043 881 |
| $C_9$ | 0,40 | 426 850 | $C_{27}$ | 0,96 | 1 016 411 |
| $C_{10}$ | 0,48 | 502 923 | $C_{28}$ | 0,91 | 961 470 |
| $C_{11}$ | 0,50 | 528 280 | $C_{29}$ | 0,87 | 920 264 |
| $C_{12}$ | 0,51 | 540 959 | $C_{30}$+ | 12,00 | 12 677 662 |
| $C_{13}$ | 1,78 | 1 881 733 | **TOTAL** | **100** | **105 724 259** |

Following the data above the **Feed Stream** is designed with reduced pressure (to 70 bar) and temperature (to 43 °C). It was observed that there are 3 phases in the feed stream – vapour (mainly because of the methane), liquid (oil) and aqueous phase (water). Therefore, the feed stream enters a 3 phase high pressure separator and afterwards a 3 phase low pressure separator. The pressure before the second separator is reduced to 5 bar, so that the stream to flash and more $CO_2$ to be separated. The two gaseous streams coming out from the two separators are mixed into one stream with a mixer, so that it can enter the **Absorber**.

The stream **Vapour 3** which is entering the absorber for removing the Carbon Dioxide is with the following mass flows:

Table 5.11 Mass flowrates of Vapour 3 stream (second simulation)

| **Component** | **Mass flowrate (kg/d)** |
|---|---|
| $CO_2$ | 262 796,25 |
| $H_2O$ | 20 163,54 |
| $N_2$ | 74 429,79 |
| $C_1$ | 2 368 728,27 |
| $C_2$ | 88 642,89 |
| $C_3$ | 70 892,20 |
| $iC_4$ | 10 636,92 |
| $nC_4$ | 23 742,16 |
| $iC_5$ | 9 456,93 |
| $nC_5$ | 13 592,52 |
| $C_6$ | 11 206,41 |
| $C_7$ | 5 311,05 |
| $C_8$ | 2 930,51 |
| $C_9$ | 1 503,35 |
| $C_{10}$ | 716,66 |
| $C_{11}$ | 299,89 |
| $C_{12}$ | 138,53 |

The **Absorber** is designed to be with 18 trays, operating pressure of 70 bar and the temperature is kept at 43 °C. The MEA in solution with water (**MEA stream**) is with the following design:

- Pressure of 70 bar; Temperature of 48 °C;
- Mass flowrate – 3 740 000 kg/d;
- MEA – 14 wt% and $H_2O$ – 86 wt%;
- Enters from the top of the column.

Before **Mea Rich** stream enters the **Regeneration Column** the pressure is reduced to 3 bar and the temperature is increased to 98 °C. The column is designed to be with the following specifications:

- 18 stages with a small pressure drop of 1 bar;
- The condenser is designed to be with full reflux, pressure of 1 bar and temperature of 38 °C;
- The reboiler is with pressure of 2 bar and a duty of 6,700e+8 kJ/h.

From the bottom exits the **Lean MEA** stream which is composed mainly of $H_2O$, MEA and a very small amount of $CO_2$. The stream goes through the cross heat exchanger to exchange heat, from there to a mixer to add the make-up streams, afterwards cooler, pump and is recycled to the absorber.

From the top of the regeneration column the separated Carbon Dioxide exits. The composition of the stream **$CO_2$ recycle** can be seen in the following table.

Table 5.12 Recycled Carbon Dioxide composition

| **Pressure** | 1 bar |
|---|---|
| **Temperature** | 38 °C |
| **Component** | **Mass flowrate (kg/d)** |
| $CO_2$ | 262 042,23 |
| $H_2O$ | 7 955,94 |
| $N_2$ | 59,35 |
| $C_1$ | 3 300,11 |
| $C_2$ | 96,00 |
| $C_3$ | 53,23 |
| $iC_4$ | 0,68 |
| $nC_4$ | 1,48 |
| $iC_5$ | 0,73 |
| $nC_5$ | 1,02 |
| $C_6$ | 6,25 |
| $C_7$ | 0,40 |
| $C_8$ | 0,21 |
| $C_9$ | 0,09 |
| $C_{10}$ | 0,04 |
| $C_{11}$ | 0,01 |
| $C_{12}$ | 0,01 |
| **TOTAL** | **273 517,79** |

**SUMMARY**

The final stage simulation has been introduced in this subpoint. This stage covers the final - third 5 years of production. Like the other two stages, the data was estimated for one day during the last 5 years of production. A summary of the achieved results can be seen in the following table.

Table 5.13 Produced Carbon Dioxide and recycled $CO_2$

| | |
|---|---|
| Produced Carbon Dioxide (for a day) | 287 740 kg/d |
| Recycled Carbon Dioxide (for a day) | 262 042 kg/d |
| Efficiency percentage | 91 % |
| Purity of the recycled $CO_2$ | 95.8 % |
| Carbon Dioxide injected (for a day) | 263 000 kg/d |

From the table above, it can be concluded that during the last stage of production the most amount of $CO_2$ has been produced. The efficiency percentage is the highest compared to the other two simulations. Furthermore, in this stage the highest purity percentage has been achieved – 95.8%. Finally, the most $CO_2$ compared to what is injected, has been recycled – 99.6%.

## 5.2 Ionic Liquid Simulation

In this section of the project, simulations using the estimated data from *Table 5.1* will be made. In contrast to the previous section, where amine-water solution was used to for separating the Carbon Dioxide from the gas stream and recycle it, here ionic liquid will be used. More specifically two ionic liquids are considered for the implementation of these simulations:

1. Tetramethylammonium glycinate ([N1111][Gly]) – this ionic liquid is used for the separation of $CO_2$ in aqueous solution;
2. 1-butyl-3-methylimidazolium tetrafluoroborate – this one is used as a pure component (100%) for separating $CO_2$ from gas stream.

As mentioned already, Aspen Hysys (v 7.3) is used for the implementation of these simulations. This software (as well as others) is used in the oil and gas industry for better understanding of processes happening taking place on the production platform (onshore or offshore). Furthermore, this is an old version of the software and it does not include ionic liquid compounds in its database. The main reason for that is because ionic liquids are still on a laboratory level and are not tested in a real production field.

However, during an extensive research the following papers [25][26][27][28][35] were reviewed and a good knowledge and data was taken from them. The data found in the papers was necessary for making hypothetical ionic liquid components in Hysys. Both above mentioned components, were made in the software as hypothetical components and were tried for removing $CO_2$ in an absorber unit.

As a fluid package the Peng-Robinson was chosen based on [35]. The units in the simulation are the same, which are used in the amine gas sweetening simulations. It is so, because the ionic liquid process is also from the type absorber/stripper.

Unfortunately, using the same data as for the other simulations, but as a separation component - 1-butyl-3-methylimidazolium tetrafluoroborate (which is used as pure) the absorber unit was unable to converge at any properties. Even at some point it started to close on its own after some properties were imported. Therefore, non-date can be provided for the separation of $CO_2$ with the use of 1-butyl-3-methylimidazolium tetrafluoroborate. Possible reasons for this unfortunate development could be that the information provided for this specific component is not enough and the software cannot solve the mathematical equations for converging the Absorber column.

However, the second component (Tetramethylammonium glycinate ([N1111][Gly])) which is used in aqueous solution has partly converged the absorber and the regeneration column. That means that the reaction is proceeding but the received results are not accurate. Hence, the results received for the $CO_2$ recycled stream (exiting the top of the absorber) can be seen in *Table 5.14.*

Table 5.14 $CO_2$ recycle stream using ionic liquid compound

| | |
|---|---|
| Produced Carbon Dioxide (for a day) | 114 637 kg/d |
| Recycled Carbon Dioxide (for a day) | 12 718 kg/d |
| Efficiency percentage | 11.1 % |
| Purity of the recycled $CO_2$ | 23.17 % |
| Carbon Dioxide injected (for a day) | 234 100 kg/d |

The data above is based on the production data for the first 5 years of production. It can be seen that the results are very unsatisfying and cannot even be compared with the amine simulations. Only 11.1% of the $CO_2$ that is originally produced is recycled and furthermore the stream consists of big amounts of Methane, Ethane, Propane, Water and others. On the other hand, the stream that must be recycled back to the absorber was with a content of $CO_2$, Methane, Ethane and etc.

Based on the received results for the first stage of production the other stages were not simulated. The main reason is that even if the simulations partly converge that doesn't mean that the received results would be accurate.

During a research, looking for a solution to this problem, in an online forum (www.cheresources.com) used by professionals in the oil and gas industry, as well as students studying in that field was found that **Aspen Plus** is capable of converting such kind of simulation (using ionic liquids). However, there isn't a license provided for this software, therefore I was unable to test its truthfulness.

# 6. Discussion and Conclusion

The main aspects of this project were to make a case study with $CO_2$ injection into a reservoir and to achieve a reasonable production flowrates and composition. Furthermore, after the production properties are estimated a separation process had to take place for the recycling of the Carbon Dioxide back to the reservoir. For this purpose two different processes were selected – amine gas sweetening and ionic liquids and simulations in Aspen Hysys were conducted with them.

The selected reservoir is relatively small and is situated in continental USA, Texas. The composition of the reservoir is of heavy oil and it has been treated with water flooding as a primary production. During the 9 years of production 22% from the original oil in place have been produced. This field was selected for $CO_2$-EOR injection and was considered that the production life will take place for 18 years. Therefore, the case study was divided into three stages – first 5 years of production, second 5 years of production and third 5 years of production. For all 3 periods/stages simulations have been made with the use of Aspen Hysys.

The composition for the 3 stages was calculated based on the initial reservoir composition (after the water flooding), as well as on the oil still in place and the remaining water in the reservoir after the primary production. Based on these criteria the mass flowrate for each component was calculated in kg/d. Furthermore, based on the fact that the $CO_2$-EOR is continuous miscible injection, the production flow was assumed.

The first three simulations were made with amine gas sweetening process. The process is well known and extensively used in the oil and gas industry. The results from the simulations showed that is a good method for the separation of $CO_2$ from gas streams with low Carbon Dioxide content, as well as with medium and high content. The achieved results from the simulations with the use of MEA in aqueous solution can be observed in *Table 6.1*.

Table 6.1 Comparison between the three amine simulations

| | **First 5 years** | **Second 5 years** | **Third 5 years** |
|---|---|---|---|
| **Produced Carbon Dioxide (for a day)** | 114 637 kg/d | 215 761 kg/d | 287 740 kg/d |
| **Recycled Carbon Dioxide (for a day)** | 84 324 kg/d | 187 973 kg/d | 262 042 kg/d |
| **Efficiency percentage** | 74 % | 87 % | 91 % |
| **Purity of the recycled $CO_2$** | 94.8 % | 95.36 % | 95.8 % |
| **Carbon Dioxide injected (for a day)** | 234 100 kg/d | 257 800 kg/d | 263 000 kg/d |

Comparing the three amine simulations over the three different periods of the production, it can be seen that the $CO_2$ production keeps growing. At the final period of production more than 100% of Carbon Dioxide is produced from which 91% are recycled. This is almost 100% of the daily injection of $CO_2$. Furthermore, with time the $CO_2$ production rises and the statistic shows that the purity of the recycled $CO_2$ rises.

The second method for removing the Carbon Dioxide from the gas stream is ionic liquid compounds. Two different components were selected, where one of it is used as a pure component and the other is used in aqueous solution. Unfortunately, both components gave unsatisfying results. Both of them were not present in the software database it was necessary to be made as hypothetical components. Hence, with the use of the first one the absorber was unable to converge under any input properties. On the other hand with the second one (used in aqueous solution) the absorber and the stripper partly converted and it gave results which are very unsatisfying and probably wrong. Therefore, they cannot be compared to the high results achieved with the amine gas sweetening process using MEA in aqueous solution.

From the estimated production composition for the period of $CO_2$-EOR injection a total of 283 720 000 kg/d of oil were produced, which is around 40% from the oil in place after the water flooding. Together with the produced oil during the primary production a total of 53% from the OOIP (original oil in place) was produced.

During the $CO_2$ continuous injection a total of 1 377 692 tonnes were injected. From which 975 168 tonnes were recycled. These is approximately 71% $CO_2$ recycled back to the reservoir.

As a conclusion, the project “Separation and Re-Injection of CO2 in Enhanced Oil Recovery Processes” gave me a whole new insight into the production platform process. Starting from the techniques to get the Carbon Dioxide to the platform, the barriers for the implementation of such project, knowledge for miscible $CO_2$ injection and different methods for the separation of Carbon Dioxide from the gas stream and its further recycling.

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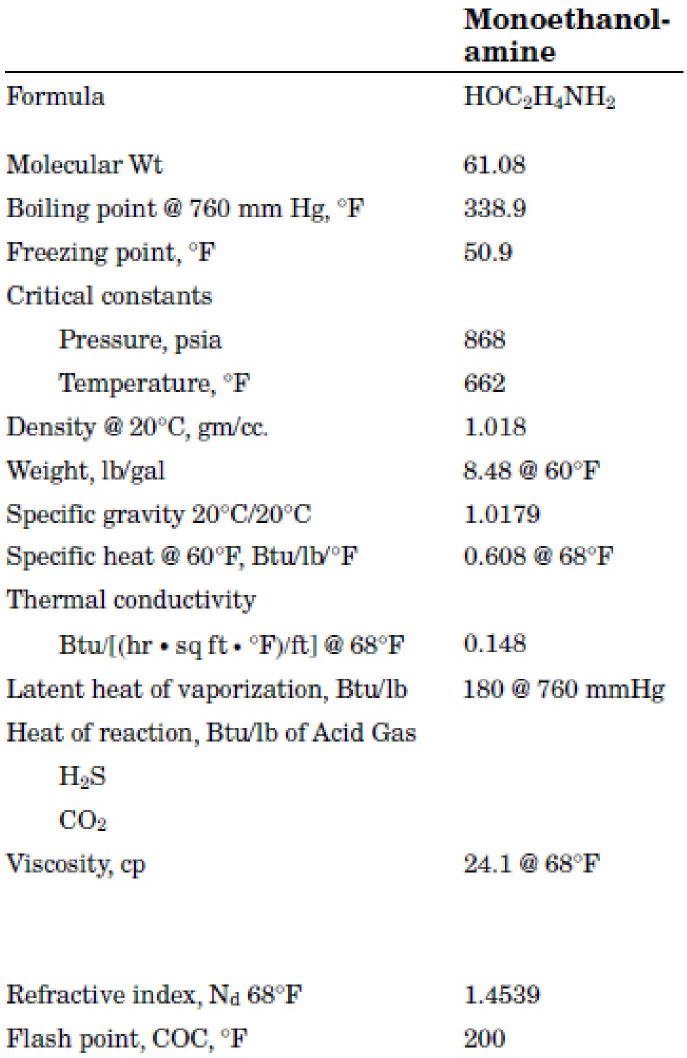
# Appendix A

## Physical Properties of MEA



| | Monoethanol-amine |
|---|---|
| Formula | $HOC_2H_4NH_2$ |
| Molecular Wt | 61.08 |
| Boiling point @ 760 mm Hg, °F | 338.9 |
| Freezing point, °F | 50.9 |
| Critical constants | |
| Pressure, psia | 868 |
| Temperature, °F | 662 |
| Density @ 20°C, gm/cc. | 1.018 |
| Weight, lb/gal | 8.48 @ 60°F |
| Specific gravity 20°C/20°C | 1.0179 |
| Specific heat @ 60°F, Btu/lb/°F | 0.608 @ 68°F |
| Thermal conductivity | |
| Btu/[(hr • sq ft • °F)/ft] @ 68°F | 0.148 |
| Latent heat of vaporization, Btu/lb | 180 @ 760 mmHg |
| Heat of reaction, Btu/lb of Acid Gas | |
| $H_2S$ | |
| $CO_2$ | |
| Viscosity, cp | 24.1 @ 68°F |
| Refractive index, $N_d$ 68°F | 1.4539 |
| Flash point, COC, °F | 200 |

# Appendix B

## First stage simulation with MEA in aqueous solution